

# PRACTICAL METHODS OF INORGANIC CHEMISTRY

BY

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## P R E F A C E

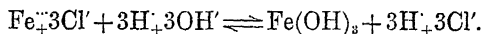
IN the training of chemists great attention is always paid, in organic chemistry, to preparative work, but for some reason or other this class of work has been very largely neglected in the teaching of inorganic chemistry. Whether this is due to a mistaken idea that the inorganic compounds are very easy of preparation, or to the difficulty of systematising inorganic chemistry, it is hard to say, but at any rate the fact remains that if a student is called upon to prepare an inorganic compound, he is very often unable to do so.

It will generally be found that students are much more interested in organic than in inorganic chemistry, because they have prepared the organic compounds, and they therefore have a better understanding of their nature and properties. My own experience is, and I am sure it is shared by others, that when students have done inorganic preparatory work they become less mechanical and take a more intense interest in the work than when inorganic chemistry is simply represented by a laboratory course of analysis and the cramming up of a text-book of combined theory and manufacturing processes.

It is because I have felt the need of a text-book on Inorganic methods of Preparation for my students, that

I have prepared this little book. All the experiments which are included in it have been tested in my own laboratories, and the methods described are those which have been found to give satisfactory results. As far as possible I would recommend that the preparations be carried on concurrently with the Qualitative Analytical Course. Thus, for example, the student might prepare the silver nitrate required for the reactions of silver, from a silver coin, and the magnesium sulphate for the magnesium reactions, from magnesite or dolomite.

Perhaps attention should be drawn to the way in which the ionic equations have been expressed, with the small + sign to denote ionic dissociation; *e.g.* on p. 45 the hydrolysis of ferric chloride is written



The reason for thus writing the equation is, that although the substance may be ionised in solution, it is difficult to imagine that there is absolutely no connection between the parts of the molecule. If we imagine the attractive forces which hold the atoms together in molecule are in the form of Faraday tubes of attraction or force, then we may imagine that in solution the tubes of force become strained—owing probably to the tendency of the individual atoms to unite with the solvent—and that therefore the substance is in a receptive condition to react and exchange atoms or groups of atoms (ions) with another substance in a similarly strained condition. If, on the other hand, it is preferred to look upon ions in



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solution as leading an absolutely independent life, then there is also no objection to the + sign because 'the properties of a solution are represented by the sum of the properties of its ions.'

For help in working through the experimental part of the book I am much indebted to Messrs. H. D. Law, B.Sc., F. B. Hart, B.Sc., and A. J. Hale; and to Mr. W. C. Prebble for most of the diagrams. I also desire to thank Mr. T. D. Morson for information upon certain methods which are employed on a commercial scale.

F. M. P.

LONDON, *June 7*, 1906.

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## CHAPTER I

### INTRODUCTION

FILTRATION.—In filtering care must always be taken to have the filter-paper fitting closely to the walls of the funnel, and it should invariably be first moistened with water or with the solution which is to be filtered through it and pressed into position, so that no air can be drawn down the sides between the paper and the funnel.

As far as possible precipitates should be washed by decantation before being transferred to the filter-paper, and unless caustic alkali or strong acid is present, in order to avoid loss of the substance, the solution which is being decanted off is poured on to the filter-paper. In pouring a solution on to a filter-paper it is advisable to hold a glass rod against the side of the beaker or other vessel containing the solution, to direct the stream of liquid against the sides of the paper. It is also often advantageous to slightly grease the outside rim of the pouring vessel in order to prevent the liquid running down the outside of the vessel.

The filter-paper must always be slightly below the edge of the funnel and the liquid never allowed to rise above the edge of the paper. When possible, always filter solutions hot, because hot solutions filter much more rapidly than cold ones.

When a substance is only soluble with difficulty in

a cold solvent, but is readily soluble when the solvent is hot, crystallising out very rapidly, however, as the

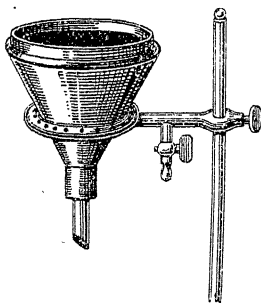


FIG. 1.

temperature falls, the solution should be filtered through a water-jacketed funnel. In fig. 1 such a funnel, which is surrounded by a ring burner so that the solution may be kept hot during filtration, is illustrated.

In some of these funnels the hot water comes in direct contact with the glass funnel. These are not to be recommended, because the funnel is apt to

break, and it is rather difficult to fix them so that no leak takes place. It is always better to use double jacketed funnels.

**VACUUM FILTRATION.**—In order to filter rapidly and to wash the substances satisfactorily, vacuum filters are often employed. When small quantities of substance are to be filtered, a porcelain disc is fitted into a funnel as shown in fig. 2. The filter-paper is carefully cut to the requisite size and spread over the plates so that the edges of the paper turn up about 3 m.m. and make even contact with the sides of the funnel; the tube of the funnel being passed through a rubber stopper and thus fixed into a filtering-flask. The Buchner funnel, illustrated in fig. 3, is however, much more satisfactory, and

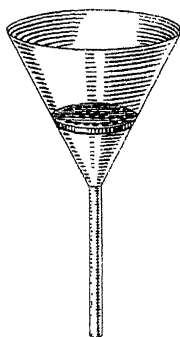


FIG. 2.

can be obtained in a variety of sizes. It is a porcelain funnel with a perforated bottom, which is fixed by means

of a rubber stopper into a filtering-flask. A piece of filter-paper is then placed so as to completely cover the perforated bottom of the funnel, which is then ready for use.

Generally water-pumps are employed for vacuum filtration. Such a pump of glass is illustrated in fig. 4. When the pressure of water is not sufficient to cause a good vacuum, a long lead pipe of narrow bore may be attached to the bottom of the pump at the water outlet. If this pipe is about 35 feet long and of such an internal diameter that the water 'cores,' that is, forms homogeneous lengths between which the air

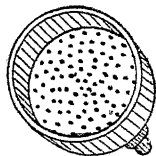


FIG. 3.

is drawn down, then, even with a small initial water pressure, an almost perfect vacuum can be obtained. Of course it is only possible to adopt this arrangement when the laboratory is at the top of a high building.

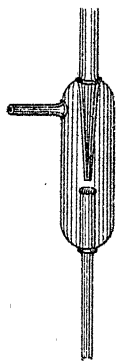


FIG. 4.

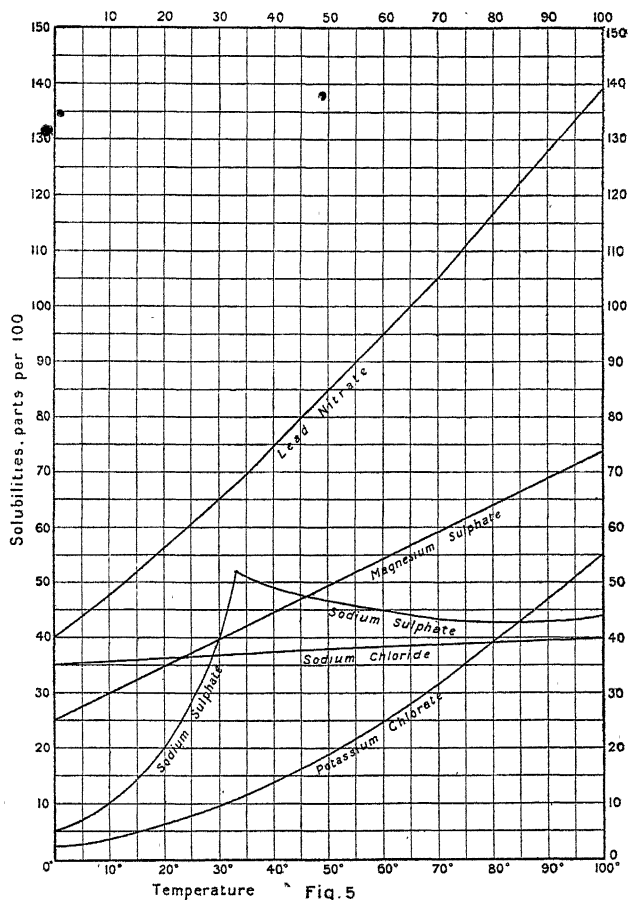
**SOLUBILITY AND CRYSTALLISATION.**—Many solid substances when brought into contact with water pass into solution, some with great ease and to a very large extent; others more slowly and only in the presence of a relatively large quantity of water. A substance may, however, pass slowly into solution and yet finally a solution may be obtained which contains a fairly large amount of the dissolved substance; such substances have a slow solution velocity. The solution of a substance is also very much affected by changes in temperature. Generally solids are more soluble in hot than in cold water, but this is by no means invariably the case. For every temperature there is a definite solubility equivalent for each substance, that is, there is a definite and constant ratio between the amount

of the substance dissolved and the solvent. The solubility of a substance is usually given as the amount of the substance which will dissolve in 100 parts of the solvent.

A **saturated** solution is obtained when more of the solid substance is brought into contact with the solvent than it is able to dissolve; a portion of the solid then remains undissolved. An **unsaturated** solution results when less of the solid is brought into contact with the solvent than it can dissolve at *that* temperature. Thus one may have a saturated solution of, say, sodium sulphate at 20°, but it will be unsaturated if the temperature is raised to 30°. Fig. 5 graphically represents the solubility of various substances at different temperatures. By examining the curves it will be seen that the solubility of sodium chloride is almost constant at all temperatures up to 100°, while most of the other substances show a progressive and marked increase in solubility as the temperature rises.

In general the curves are continuous, but it will be noticed that the one representing sodium sulphate shows a sharp break at 33°, and from that temperature upward the solubility shows a progressive decrease with rise of temperature. The explanation of this apparent anomaly is that we are dealing with two solubility curves. The curve below 33° is the solubility curve of hydrated sodium sulphate,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ; whereas that above 33° is the curve of anhydrous sodium sulphate,  $\text{Na}_2\text{SO}_4$ . If the hydrate is heated to 33° it loses its water of crystallisation; it is consequently only stable up to a temperature of 33°. It therefore follows that above 33° the solution cannot be in contact with the solid hydrated sodium sulphate, but must be in contact with the anhydrous salt. Other hydrated substances, but not all, show similar phenomena. For instance, the curve produced by manganese sulphate shows a break between 54° and 64°. At 54° the solubility is

75.3 per cent., but at 64° it is only 61.5 per cent.; this



is due to the fact that the hydrate  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  is not stable above 60°.

Substances cannot be caused to crystallise unless the solution is *supersaturated*. It does not, however, follow that a substance will crystallise out even when the solution is supersaturated. Before crystallisation takes place, it generally requires some nucleus for the substance to commence to crystallise from. As soon, however, as the crystallisation commences it continues until the solution is saturated, but not supersaturated, at the existing temperature. As a matter of fact, crystallisation will usually proceed progressively, owing to evaporation, unless indeed there be any great rise in temperature which might cause the crystals to pass into solution again.

EXPERIMENT.—Prepare a supersaturated solution of magnesium sulphate by adding the crystallised salt to 50 c.c. of boiling water until no more is dissolved. Then, keeping the solution boiling, add small quantities of water until no solid remains, and stop the neck of the flask with cotton wool. Stand on one side to cool; when quite cold, open the flask and drop in a minute fragment of crystallised magnesium sulphate. Immediately, from the point at which the solid substance touched the solution, crystals will commence to form, and in a very short time the whole of the solution will become a solid mass. A considerable rise in temperature will also be noticed. If the flask is kept with the wool in it and is not moved, the solution which is so much supersaturated may often be kept for days without crystallisation taking place, but vibration or a little piece of dust falling into the flask may be sufficient to cause crystallisation to ensue.

In order to crystallise a substance it is generally dissolved to saturation or nearly to saturation in the hot fluid from which it is to be crystallised, and the solution is then allowed to cool slowly.

The slower crystallisation takes place the larger the



crystals and the better the crystalline form. In order to obtain really good crystals, the vessel in which the solution has been caused to take place is allowed to cool upon a slowly cooling water-bath. Or the crystallising dish may be placed in a wider dish and surrounded with cotton wool, the top being closed with a clock glass.

When very large crystals are desired they may be obtained by removing one or more of the best formed crystals from the solution. They are then placed in another dish and the mother-liquor is poured over them. If on standing other crystals separate out, the large crystals must be again removed and the mother-liquor again poured over them, this process being continued from day to day until crystals of sufficient size have been obtained. A good method to obtain crystals of considerable size is to place a glass rod across a beaker and from this to hang a piece of cotton down nearly to the bottom of the solution. The bulk of the crystals will then collect upon the cotton, the rough surface of which forms nuclei for the commencement of the crystallisation. This method is employed on a large scale, as, *e.g.*, in the preparation of barley-sugar. Another method is to support glass rods below the surface of the solution from which crystals are to be obtained; the crystals then adhere to the glass rods, from which they are readily separated.

For analytical purposes it is generally advisable to obtain the crystals as small as possible, because in this case the mother-liquor is easily washed out and there is no chance of its becoming enclosed in the crystals, as is sometimes the case with large crystals. In order to obtain small crystals a saturated hot solution is prepared, and the beaker containing the solution is placed in a vessel of cold water, the solution being continuously stirred while cooling.

If a solution is too dilute for crystallisation to take place,

it is evaporated down on a water-bath until upon dipping a glass rod into the solution and cooling it, crystals are deposited upon it. Students generally make the mistake of concentrating the solutions too much. As a result, on cooling the solution, they obtain a powdery mess which is generally very impure. If by accident the solution is evaporated too far, the only thing to be done is to add more of the solvent and redissolve it, after which it is evaporated to the required concentration.

Certain substances, when left to crystallise, 'creep' up the sides of the crystallising dish. This phenomenon is the same as that of *efflorescence*, and is shown, among other substances, by ammonium salts and by sodium carbonate. It is caused by the evaporation of the solution and the deposition of crystals upon the walls of the containing vessel. Capillarity then causes a small portion of the solution to creep up over the crystals, and from this, in turn, crystals are deposited so that by degrees the crystals creep right out of the dish, and thus much substance may be lost; the crystals also are not pure. In order to prevent this creeping, the sides of the crystallising dish may be very thinly smeared with vaseline or oil, just above the level of the solution. Great care must be taken not to render them so greasy that particles of oil or grease float in the solution.

SUBLIMATION.—Certain substances, such, for example, as aluminium chloride (see p. 85) and iodine, cannot be crystallised or are more readily purified by sublimation. Sublimation is a similar operation to that of distillation, the substance being converted into vapour which upon cooling solidifies. By means of sublimation a volatile substance can be separated from a non-volatile impurity.

Sublimation may be carried out in various ways. The substance to be sublimed may be placed in a porcelain

basin on a sand-bath and covered with a beaker, the edges of the beaker being embedded in the sand. The top of the beaker may be kept cool by placing a crystallising dish containing cold water upon it. Another method is to place the substance in a flask, place the flask on a sand-bath, and cover the mouth with a watch-glass. On heating the substance it sublimes to the upper parts of the flask, from which it can be obtained by breaking the flask. This method is only adopted when the substance is of considerably more value than the flask.

Small quantities of substance can be sublimed in a test tube or in a porcelain crucible covered with another larger crucible holding water. A very good method is to place the substance into a boiling tube, then wrap the upper part of the tube with asbestos paper and insert it into the mouth of a bottle, so that it fits almost air-tight. The substance is then distilled from the tube into the bottle. For larger quantities, and when this substance is readily volatile, a retort may be used.

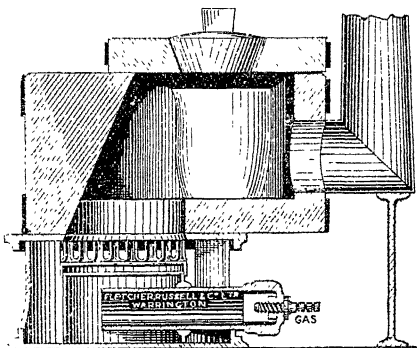


FIG. 6.

**FUSION AND IGNITION.**—Fusion or ignition, when only a small quantity of substance is being dealt with, is often carried out before the blowpipe or over the Bunsen burner, but with larger quantities a muffle furnace or crucible furnace must be used. Fig. 6 shows diagrammatically a

crucible furnace which will be found very useful for several of the ignitions and fusions required in this book.

### Strength of Reagents.

It is advisable always to use solutions of uniform strength,

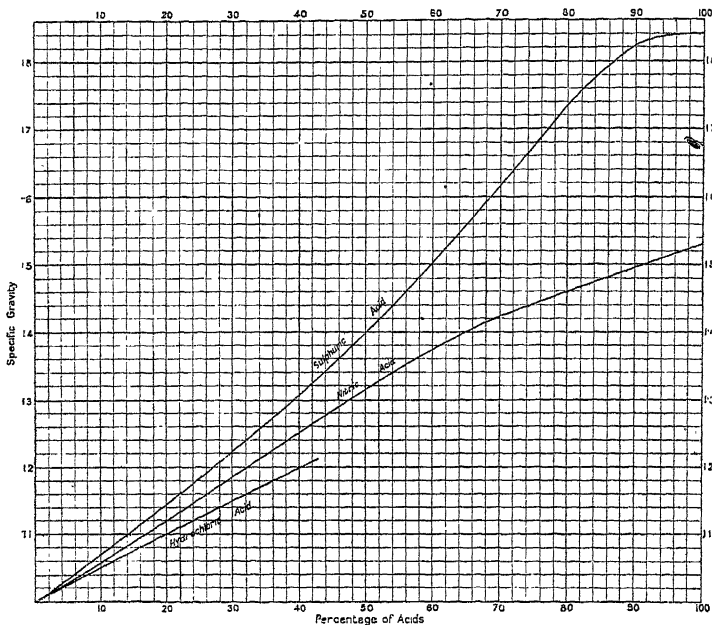


FIG. 7.

and it is best, as far as possible, to prepare them of equivalent strength. A very convenient strength for acids and bases is 4N. When acids and bases are made up in this manner it is much easier to neutralise them than when the strengths are made up at random. For example, if

5 c.c. of an acid of 4N. strength has been employed, it will be neutralised by the addition of a 5 c.c. of a 4N. solution of an alkali. As strong acids are better not to be weighed upon the balance, at any rate by beginners, it is better to measure them. From the curves on fig. 7 for sulphuric, hydrochloric, and nitric acid, there is no difficulty in obtaining the desired quantity of these acids by measurement provided the specific gravity is known, and this is easily found by means of an hydrometer. The vertical line gives the specific gravities and the base line the percentage strength of the solution.

Suppose, for example, that the sp. gr. of a solution of sulphuric acid is 1.4, the strength of the acid can be found by taking the number 1.4 on the vertical line and following the horizontal line until it is cut by the sulphuric acid curve. On tracing from this point an imaginary line perpendicularly down to the base, we find that an acid of this sp. gr. contains 62.3 grm. of  $H_2SO_4$  in 100 c.c. of solution.

The quantities required to make up a few of the more important of the reagents will be found at the end of the book.

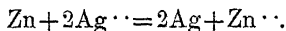
## CHAPTER II

### GENERAL PREPARATIONS AND METHODS

#### Pure Silver from a Silver Coin.

CLEAN a threepenny bit, carefully weigh it and place in a beaker of 100 c.c. capacity, add 15 c.c. nitric acid diluted with an equal bulk of distilled water, and cover with a clock glass. As soon as the vigorous reaction has ceased and the whole of the coin has gone into solution, dilute with about 30 c.c. of distilled water and add dilute hydrochloric acid, until, on allowing the precipitate of silver chloride to settle and then adding a drop of hydrochloric acid, no further precipitate is produced. A large excess of hydrochloric acid should not be added, because silver chloride is distinctly soluble in an excess of the acid or in excess of chlorides such as magnesium or sodium chloride.

Filter off the silver chloride and well wash with hot water. Now wash the precipitate off the filter-paper into a beaker and add *just sufficient* of a solution of potassium cyanide to dissolve all the silver chloride, and then add a small quantity of zinc dust to the solution. The zinc takes the place of the silver and passes into solution, the silver being precipitated out thus:—



When all the silver has been thrown out, which can be

told by no further action taking place on the addition of another small quantity of zinc dust, pour off the solution, wash with a little water by decantation, and then allow to stand in contact with a little dilute sulphuric acid until any remaining zinc is dissolved. Transfer to a tarred filter-paper, well wash with water, and dry in the steam oven. Cool and weigh. A sterling silver coin contains 92.5 per cent. of silver; the result obtained should be very close to this.

SILVER NITRATE may be obtained from the silver thus produced by dissolving in a small quantity of nitric acid, evaporating to dryness on the water-bath, dissolving in water, and evaporating to crystallisation.

### Lead Nitrate from Litharge.

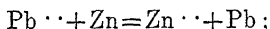
Take 15 grm. litharge, place in a beaker or conical flask, add about 25 c.c. water, and then 12 c.c. strong nitric acid, and warm on the sand-bath until all the litharge has dissolved and a clear solution is obtained. If the litharge is not all acted upon, then add a few drops more nitric acid until it completely dissolves, but be careful not to add a large excess. On cooling, the lead nitrate crystallises out. Calculate how much lead nitrate should be formed, and then ascertain how much has been obtained. By careful evaporation of the mother-liquor almost the whole of the lead nitrate can be obtained in the crystallised form.

### Metallic Lead.

Prepare a strong solution of lead acetate,<sup>1</sup> put it in a beaker, and then tie a weighed piece of zinc to a glass rod with a piece of cotton, and hang it into the solution.

<sup>1</sup> Lead acetate can be prepared by dissolving litharge in warm acetic acid in a similar manner to that in which lead nitrate is prepared.

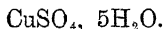
The lead will be precipitated upon the zinc in the form of beautiful spangles. As, however, the lead becomes deposited the zinc goes into solution, and if left long enough, only lead will remain. As it does not matter what salt of lead is used, the equation may be written as follows :—



the lead, which at first is present as an ion, assuming the molecular form and the zinc going over into the ionic condition.

Lead so deposited is usually called a *lead tree*. Remove the lead from any remaining zinc, wash it with water, and dry by pressing it between filter-paper. It can now be melted into a globule by heating it before the blowpipe on a piece of charcoal. Ascertain whether the quantity of lead obtained corresponds to the zinc which has gone into solution. If the whole of the zinc has not gone into solution it will be necessary to weigh the part which remains.

### Copper Sulphate.



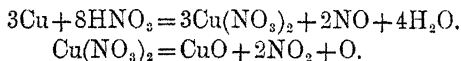
Copper sulphate can be prepared by dissolving copper in strong sulphuric acid, but as copper sulphide is formed at the same time owing to secondary reactions, it is not a good method to adopt in the laboratory. The reactions which take place may be represented as follows, being caused by the reducing action of the hydrogen at the high temperature and concentration of the acid :—

- (i)  $\text{Cu} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + 2\text{H}.$
- (ii)  $2\text{H} + \text{H}_2\text{SO}_4 = \text{SO}_2 + 2\text{H}_2\text{O}.$
- (iii)  $8\text{H} + \text{H}_2\text{SO}_4 = \text{H}_2\text{S} + 4\text{H}_2\text{O}.$
- (iv)  $2\text{H} + \text{H}_2\text{S} + \text{CuSO}_4 = \text{Cu}_2\text{S} + 2\text{H}_2\text{SO}_4.$
- (v)  $\text{SO}_2 + \text{H}_2\text{S} = 3\text{S} + 2\text{H}_2\text{O}.$



It may, however, very readily be obtained by dissolving cupric oxide in dilute sulphuric acid. Commercial cupric oxide invariably contains a certain quantity of unoxidised copper and therefore does not completely dissolve. Further, commercial copper scale does not dissolve in dilute sulphuric acid, therefore it is better to prepare the copper oxide by first forming the nitrate and then igniting it.

Dissolve 5 gramm. metallic copper in 30 c.c. of a mixture of equal volumes of concentrated nitric acid and water. When the copper has completely dissolved, place the solution in a weighed evaporating basin and evaporate to dryness. When quite dry, ignite gently over the Bunsen burner until no more fumes of oxides of nitrogen are given off, and the resulting product is a homogeneous black powder.



Weigh the copper oxide and see whether it agrees with the quantities shown by the equation.

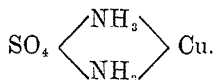
Now warm the cupric oxide with 55 c.c. of 4N. sulphuric acid until it has all gone into solution, and set aside to crystallise. Filter off the crystals, wash with a very small quantity of water, and dry on filter-paper. When quite dry, powder a small quantity of the crystals, weigh out about 1 gramm. on to a watch-glass and determine the water of crystallisation, first by heating to 150° until the weight is constant, and then to 200° until no further decrease in weight takes place. Before each weighing the substance must be cooled in a desiccator. From the results obtained find how many total molecules of water of crystallisation the copper sulphate has, and how many molecules are given up at the respective temperatures.

### Cuprammonium Sulphates.

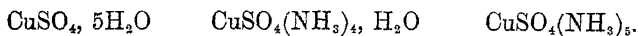
When ammonium hydroxide is added to a solution of a cupric salt, at first a greenish-white precipitate is produced, which, however, dissolves on the addition of a further quantity of the ammonium hydroxide. This blue-coloured solution is due to the formation of a cuprammonium salt,  $\text{CuSO}_4(\text{NH}_4)_4, \text{H}_2\text{O}$ . It can be obtained in the crystalline state by the addition of alcohol.

Powder 10 grm. copper sulphate and dissolve it in 40 c.c. distilled water, now add ammonium hydroxide to the solution until the precipitate at first formed is completely dissolved and a pure blue solution is obtained. Allow to cool and carefully run a layer of alcohol about 1 cm. deep on to the surface of the solution and allow to stand overnight. Deep blue crystals separate out, which may be filtered off and dried on a porous plate. They gradually decompose on keeping.

By passing dry ammonia gas over anhydrous copper sulphate a blue powder is obtained having the formula  $\text{CuSO}_4 \cdot 5\text{NH}_3$ . Both of these compounds split up when heated to  $200^\circ$  into  $\text{CuSO}_4 \cdot 2\text{NH}_3$ , which may be looked upon as ammonium sulphate in which two atoms of hydrogen are replaced by copper.



The other two compounds from which this is obtained may be looked upon as copper sulphate in which the molecules of water are replaced by ammonia, thus:—



Other copper salts form similar compounds.

**Zinc ammonium** compounds are produced in a somewhat similar manner; for example, the compound  $\text{ZnSO}_4(\text{NH}_3)_2 \cdot \text{H}_2\text{O}$  is produced when ammonia gas is conducted into a warm, nearly saturated solution of zinc sulphate until the precipitate at first produced is dissolved. It is obtained as a whitish crystalline powder on cooling.

The salt  $\text{ZnSO}_4(\text{NH}_3)_4 \cdot 4\text{H}_2\text{O}$  is obtained by allowing the solution of the above salt to slowly evaporate at ordinary temperatures; whereas  $\text{ZnSO}_4(\text{NH}_3)_6$  is produced when dry ammonia gas is led over heated dry zinc sulphate. It forms a white powder, which deposits  $\text{Zn}(\text{OH})_2$  on addition of water.

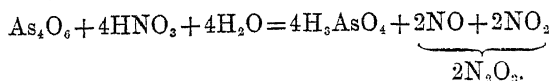
Chromium and cobalt also form a large series of amino compounds, some of which are of extreme complexity, but they are of great interest; for their preparation the original papers must be studied. An account of some of them can be found in Roscoe and Schorlemer, vol. ii.

### Sodium Arsenate.

Take 20 grm. arsenious oxide ( $\text{As}_2\text{O}_3$ ), place in a flask, and cover with 30 c.c. nitric acid, sp. gr. 1.38; it is better to use the lump arsenious oxide broken into a rough powder, rather than the finely powdered product, as the reaction is then not so vigorous. Place the flask on a water-bath and heat until no more brown fumes are given off. Pour off from any unchanged arsenious oxide and evaporate nearly to dryness, dilute with water, and repeat the evaporation in order to drive off the excess of nitric acid. Again dissolve in about 30 c.c. water and exactly neutralise with sodium hydroxide and set aside to crystallise. The salt so obtained has the formula  $\text{Na}_2\text{H}_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ . The salt  $\text{Na}_2\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  is obtained when excess of sodium

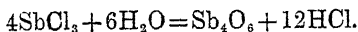
hydroxide is added to a solution of arsenic acid. Either of these salts can be used to show the reactions of the arsenates.

When arsenious oxide is heated with a nitric acid it is oxidised to arsenic acid and the nitric acid is reduced to nitrogen trioxide.

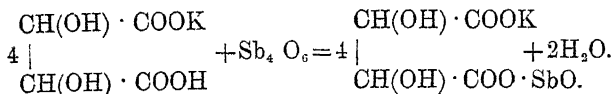


### Antimonious Oxide and Tartar Emetic.

Take 15 grm. antimony trichloride (for preparation see p. 77) and grind it up to a powder, then suspend it in boiling water. A white precipitate of antimonious oxide is produced. Filter off the precipitated oxide, and wash it first with a hot dilute solution of sodium carbonate and then with hot water.



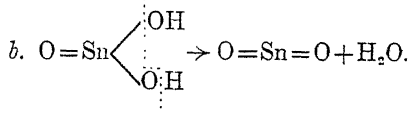
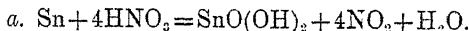
In order to prepare tartar emetic from the antimonious oxide, dissolve 13 grm. potassium hydrogen tartrate in water and add the oxide to the boiling solution; on cooling, antimonyl potassium tartrate separates out in the form of small crystals containing  $\frac{1}{2}$  mol. water of crystallisation.



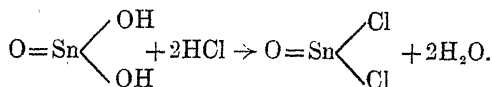
As tartar emetic dissolves in water without forming antimony oxychloride, it is a very useful substance to employ when carrying out the reactions of trivalent antimony.

### Stannic Oxide.

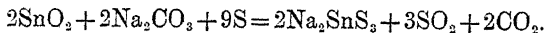
When metallic tin is acted upon by strong nitric acid it is converted into **metastannic acid**, which upon being strongly heated loses water and is converted into stannic oxide.



Metastannic oxide, although not soluble in strong hydrochloric acid, is converted by it into metastannic chloride, which is soluble in water, so that by treating it with hydrochloric acid, then pouring off the excess of acid and adding water, solution can be obtained.



The oxide after ignition cannot be dissolved in acids but can be converted into the soluble thiostannate by fusion with a mixture of sulphur and sodium carbonate.



If, therefore, in analysis, the dry reactions indicate tin and the substance is found to be insoluble, probably stannic oxide is present, and the best method to get it into solution would be fusion with sulphur and sodium carbonate.

It is an instructive exercise to carry out the above operations, also to determine the equivalent weight of tin.

*Equivalent of Tin.*—Weigh a porcelain evaporating basin, place 1 grm. tin in it, and then just cover it with water,

and add about 5 c.c. of concentrated nitric acid, cover with a funnel, and allow the rather vigorous reaction to proceed. As soon as the reaction has finished, wash the funnel into the basin (the funnel is employed to prevent loss by spurting) and evaporate to dryness on the water-bath. When it is quite dry, heat strongly over the Bunsen flame, cool, and weigh. Again heat to low redness, and if, after cooling and again weighing, no change in weight has taken place, the operation is finished. Enter the result as follows:—

*Equivalent weight of Tin.*

|                                    |   |  |
|------------------------------------|---|--|
| I. Weight of basin + tin           | = |  |
| Weight of basin                    | = |  |
| Weight of tin                      | = |  |
| <hr/>                              |   |  |
| II. Weight of basin + oxide of tin | = |  |
| Weight of basin                    | = |  |
| Weight of $\text{SnO}_2$           | = |  |
| <hr/>                              |   |  |

Now if  $x$  gram. of tin took up  $y$  gram. of oxygen to form stannic oxide, how much tin would take up 8 gram. of oxygen? Now the equivalent of oxygen compared to hydrogen is as 8 to 1, therefore by this method we shall find how many gram. of tin are equivalent to 1 gram. of hydrogen.

But we can also determine the atomic weight by assuming that stannic oxide is tetravalent and by taking the atomic weight of oxygen as 16. The atomic weight of oxygen having been very carefully determined is now employed as the standard from which atomic weights are calculated, and for this purpose the atomic weight has been fixed at 16. By altering the equation, and as tin is here tetrad, employ-

ing 32 instead of 8, the atomic weight will be obtained; see whether it agrees with the number given on p. 146.

### Equivalent of Magnesium.

The equivalent of magnesium compared to hydrogen can be found by measuring the volume of hydrogen given off when a weighed quantity of the metal is acted upon by an acid. The apparatus illustrated in fig. 8 may be

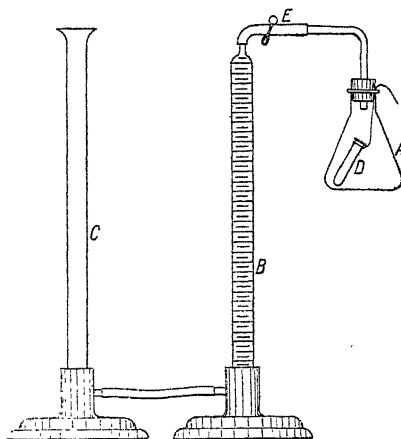


FIG. 8.

employed. A is a flask of about 100 c.c. capacity, fitted with a rubber stopper, through which passes a bent glass tube, and by means of which it is connected to the measuring tube, B. The measuring tube is connected by rubber tubing with the levelling tube, C. A small test tube, holding about 4 or 5 c.c., is suspended in the flask, A, with a piece of cotton.

In order to carry out a determination, a piece of magnesium wire, weighing *not* more than 0.08 to 0.085 gm., is accurately weighed and placed in the flask, A, and then about 30 c.c. of water is added. The tube, D, is filled about two-thirds with concentrated hydrochloric or sulphuric acid, and is held in position by the cotton, while the rubber stopper is tightly fixed in the flask. It is a good thing to soak the cotton in oil, as this then prevents air being sucked in. Before connecting the glass tube with the rubber tube, the clip on E is opened, and by raising the tube, C, which is full of water, the measuring tube, B, is filled. The clip is then closed and the flask, A, connected to the rubber tube, E. The clip is then again opened, and the level of the water in B noted by bringing the level of the water in the tube, C, to that in B. This precaution is necessary, because, when flask A is connected to B, a slight compression of the air in A takes place, and on releveing, it will generally be found that the level of the water in B is about 1 cm. lower than at first. When the levels are adjusted, the tube, C, is placed rather lower than B, and the acid in the test tube caused to run over into the flask, A, by tilting the flask on one side. Hydrogen is evolved and passes into B, forcing the water out into C. When no more gas is evolved, allow to stand for twenty minutes to half an hour, adjust the level of the water in C and B, and read off the volume of the gas. Note the temperature, and in order that the temperature reading may be correct, hang the thermometer on to B for about ten minutes before reading it. The height of the barometer must also be taken. By means of these data the volume can be reduced to N.T.P.; but another very important correction must also be made, the correction for the tension of aqueous vapour. This number can be found by consulting the table on p. 145, and must be subtracted



from the observed barometer height. The entries should be made as follows, the numbers here given being taken from an actual experiment :—

|                                |       |             |
|--------------------------------|-------|-------------|
| Weight of magnesium taken,     | . . . | 0.0884      |
| Barometer, . . . . .           | . . . | 764 m.m.    |
| Temperature, . . . . .         | . . . | 17°         |
| Volume of hydrogen gas, . . .  | . . . | 89.1 c.c.   |
| Tension of aqueous vapour, . . | . . . | 14.395 m.m. |

$$v_0 = \frac{v \times (p - T) \times 273}{(760 \times 273 + t)},$$

where  $v_0$  is the volume at normal pressure and temperature,  $v$  the observed volume,  $p$  the barometer height,  $T$  the tension of aqueous vapour, and  $t$  the observed temperature. We obtain, therefore,

$$v_0 = \frac{89.1 \times (764 - 14.395) \times 273}{760 \times (273 + 17)} = 82.73.$$

In order to find the weight of hydrogen, this volume is multiplied by the 0.0000896, the weight of 1 c.c. of hydrogen. This weight, 0.007412, is then divided into the weight of magnesium taken, when we obtain 11.93 as the equivalent of magnesium. Now magnesium is divalent; if we therefore multiply this number by 2 we obtain the atomic weight as 23.86 compared to hydrogen as 1. This is very close to the number obtained by exact experiment—viz. 24.18.

The equivalent of zinc and of other metals which evolve hydrogen on treatment with an acid can be found in a similar manner.

### Determination of Equivalents by Replacement of one Metal by another.

It has already been found that when metallic zinc is placed in a solution of a silver salt, the zinc goes into solution and metallic silver is precipitated out (p. 12). The ratio of silver deposited for a given weight of zinc is constant. Now by experiment it is found that 32.45 parts by weight of zinc will replace 1 gram. of hydrogen from its combinations in acids or alkalis. Bearing these facts in mind, it is possible to find out indirectly the weight of silver which is equivalent to 1 gram. of hydrogen, or as magnesium will also replace silver from solutions of its salts, this metal can also be employed.

In order to determine the hydrogen equivalent of silver in this way, carefully weigh out about 0.1 to 0.2 gram. of magnesium powder. Place it in a beaker, and add to it a warm solution of about 3 gram. of silver nitrate; stir well with a glass rod for about ten minutes, then allow to stand for another ten minutes, and filter on to a filter-paper the weight of the ash of which is known. The analytical paper of Carl Schleisher and Schull yield, after burning, so little ash that its weight may be neglected. The precipitated silver must be well washed with hot water until a drop of the filtrate no longer gives a turbidity when treated with a drop of dilute hydrochloric acid. Then dry in the steam oven. Transfer as much as possible of the silver to a weighed crucible: the crucible should be placed upon a piece of glazed paper, so that if any of the silver be spilt it can readily be swept into the crucible with a camel hair brush. When as much of the silver as possible has been transferred to the crucible, wrap the filter-paper into a spill and fold round it loosely a piece of

platinum wire. Hold the loose end of the wire in such a manner that the rolled paper is directly over the crucible, and set the paper on fire with a Bunsen burner. Allow the paper to smoulder away until only a whitish ash remains, and then knock the ash into the crucible. Heat the crucible and contents to redness, cool in a desiccator, and weigh.

Enter the results thus; the numbers are taken from an actual experiment:—

|  |   |         |
|--|---|---------|
| Weight of magnesium + beaker, . . .    | = | 27.6590 |
| Weight of beaker, . . . . .            | = | 27.4880 |
|  |   | <hr/>   |
| Weight of silver, . . . . .            | = | 1.1710  |
|  |   | <hr/>   |
| Weight of crucible + silver, . . . . . | = | 10.1713 |
| Weight of crucible, . . . . .          | = | 8.6590  |
|  |   | <hr/>   |
|  |   | 1.5123  |
|  |   | <hr/>   |

Now knowing that 12.09 parts of magnesium will displace 1 gram. of hydrogen, the weight of silver which is equivalent to 1 gram. of hydrogen can be found as follows:—

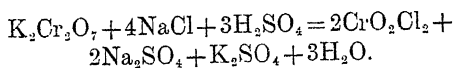
$$\frac{1.5123 \times 12.09}{0.1710} = 106.90.$$

The number found by exact experiment is 107.12.

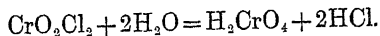
Other equivalents may be obtained. Thus, for example, zinc will replace copper, and iron will also replace copper. When care is taken very exact results can be obtained. In the case of copper it is better to employ a tarred filter-paper, because when burnt the copper adhering to the filter-paper is oxidised.

### Chromyl Chloride.

Powder 10 grm. of potassium dichromate and mix it intimately with 18 grm. sodium chloride. Place the mixture in an 8-oz. stoppered retort, and then run in 50 c.c. of concentrated sulphuric acid. Deep reddish-brown fumes are at once produced; by gently warming distil into a flask which is kept cool by being placed in water.



In a short time a heavy red fluid will have collected in the receiver. On mixing with water it is decomposed and a yellow solution of chromic acid is obtained.

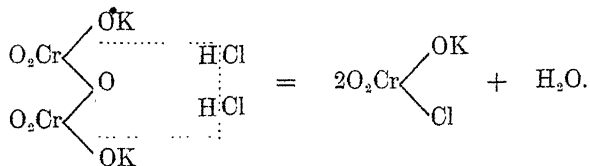


Chromyl chloride is a heavy reddish-brown liquid closely resembling bromine in appearance; it boils at  $116^\circ$ - $118^\circ$ .

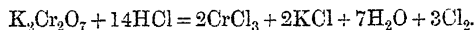
### Potassium Chromyl Chloride.

Grind up 10 grm. of potassium dichromate to a fine powder, and then add 14 grm. of concentrated hydrochloric acid, and again grind. The addition of the acid causes the potassium dichromate to cake, hence the necessity of the second grinding. Transfer the mixture to a flask and warm gently until fumes of chlorine commence to come off, then cease heating and add 15 c.c. of water. Place the brownish-red solution upon a hot-water bath, from which the source of heat has been removed, and allow to cool slowly. When cold the potassium chromyl chloride will have crystallised out in magnificent ruby red needles. Decant off the solution and wash once or twice with dilute hydrochloric acid. Allow to drain for about

quarter of an hour on a porous plate, and then transfer to an evaporating basin and heat in the steam oven for about quarter of an hour, finally transfer to a stoppered bottle.



On heating, chlorine gas is given off, in fact a mixture of concentrated hydrochloric acid and potassium dichromate is sometimes used for generating chlorine gas.



Water decomposes it into potassium dichromate and hydrochloric acid. For this reason it can only be crystallised from solutions of hydrochloric acid.

### Magnesium Sulphate.

Take 50 c.c. of 4N. sulphuric acid, place in a beaker, and add powdered magnesite ( $\text{MgCO}_3$ ) until no more is dissolved. The magnesite does not dissolve very rapidly, so that the mixture should be gently warmed on the sand-bath. When effervescence no longer takes place, filter the solution and set aside to crystallise. It may be necessary to evaporate the solution to smaller bulk before crystallisation takes place. Filter off the crystals and dry between folds of filter-paper.

Take about 1 gram. of the salt so dried and determine the water of crystallisation.

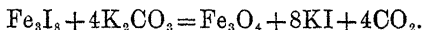
Dolomite can also be used for preparing magnesium

salts. As, however, it consists of magnesium calcium carbonate, calcium sulphate separates out and must of course be removed by filtration.

### Potassium Iodide.

Grind up in a mortar 15 grm. iodine and 5 grm. iron filings with 50 c.c. of water. Allow to stand for twenty minutes and then grind in another 5 grm. of iodine. Transfer to a flask and digest on the water-bath with 14 grm. of potassium carbonate for fifteen minutes. Filter from the precipitated oxide of iron and evaporate to crystallisation.

The first action of the iodine on the iron is to form ferrous iodide, and this is then converted into  $\text{Fe}_3\text{I}_8$ , which on boiling with potassium carbonate is converted into ferrous ferric oxide and potassium iodide.



This method is the one which is adopted on the commercial scale.

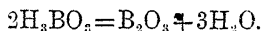
Potassium iodide is soluble in 0.7 parts of water and in 2.5 parts of alcohol.

### Boric Acid.

Dissolve 50 grm. powdered borax,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , in 200 c.c. boiling water and then add 40 c.c. concentrated hydrochloric acid. Allow to stand overnight and filter off the precipitated boric acid. Wash with a little cold water, dry on a porous plate, and then at  $120^\circ$  for an hour in order to expel the last traces of hydrochloric acid. Recrystallise from boiling water.

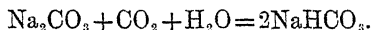


A further quantity of crystals can be obtained by concentrating the mother-liquors. Boric acid crystallises in pearly leaflets which upon being strongly heated lose water and fuse to a glassy mass of boron trioxide.

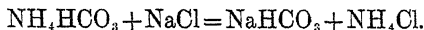


### Sodium Bicarbonate.

Sodium bicarbonate is formed when carbon dioxide is passed into a solution of normal sodium carbonate until the solution no longer gives an alkaline reaction to litmus paper.



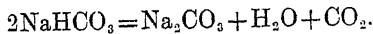
Commercially it is, however, generally prepared from sodium chloride by what is called the *Ammonia Soda Process*. The process depends upon the reaction of a strong solution of sodium chloride upon ammonium hydrogen carbonate, with formation of sodium bicarbonate and ammonium chloride.



The sodium bicarbonate being less soluble than the ammonium chloride, separates out, and the ammonium chloride remains in solution.

Dissolve 100 grm. sodium chloride in 300 c.c. of water, stand the solution in a basin surrounded with ice, and pass in ammonia gas until the solution is saturated. If the solution is, as will probably be the case, turbid, filter it into a narrow glass jar of about 450-500 c.c. capacity. Through a rubber stopper which fits the jar tightly pass a wide glass tube reaching nearly to the bottom of the jar. Connect the glass tube with a Kipp apparatus for generating carbon dioxide, loosen the rubber stopper and pass a rapid

stream of carbon dioxide into the solution, so that all the air is driven out from the top of the liquid. When this has taken place close the jar with the rubber stopper and leave in connection with the carbon dioxide apparatus. The gas will be rapidly absorbed and will bubble up through the liquid. If the gas does not pass in freely, there is probably some air above the solution; in this case again loosen the stopper and pass the gas rapidly for a few minutes before closing it again. The apparatus should then be left in contact with the ammoniacal solution overnight; by this time the solution will probably be saturated and the sodium bicarbonate will have collected at the foot of the jar. Filter it off and wash with a small quantity of ice-cold water. Then spread on a porous plate to dry. Sodium bicarbonate cannot be dried at high temperatures, because it splits up into normal sodium carbonate, carbon dioxide, and water.





## CHAPTER III

### SALTS

#### Pure Sodium Chloride.

COMMON salt always contains a considerable amount of impurities such as traces of iron and small quantities of magnesium salts, which latter cause it to deliquesce in a moist atmosphere.

In order to purify the salt it is dissolved in water and treated successively with milk of lime, barium chloride, and sodium carbonate. By this means any salts of the heavy metals are thrown out as hydroxides, sulphates as barium sulphate, and any excess of barium and lime removed by the addition of the sodium carbonate. Finally, advantage is taken of the fact that sodium chloride is only very slightly soluble in a strong solution of hydrochloric acid, whereas any magnesium chloride which may be present remains in solution.

PROCESS.—Dissolve 200 grm. common salt in 600 c.c. water, heat to boiling and add 6 grm. of slaked lime, which has been made into a thin cream: now add 20 c.c. of a normal solution of barium chloride and allow the precipitate to settle. Add a solution containing 6 grm. sodium carbonate, and after standing for a few minutes, filter. Now evaporate the solution to about 450 c.c., cool and pass in hydrochloric acid gas until the solution is

saturated. As the hydrochloric acid gas is passed in, the sodium chloride gradually commences to fall out in the form of very fine crystals.

In order to prevent the solution being sucked back into the hydrochloric acid generator, should the evolution of gas cease, the apparatus should be fitted up as illustrated in fig. 9.

A is a filter flask which is about one-quarter filled with concentrated commercial hydrochloric acid. It is closed

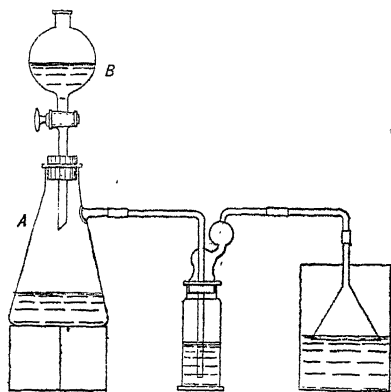


FIG. 9.

at the top with a rubber stopper through which is passed a dropping funnel, B, containing concentrated commercial sulphuric acid. The tubulus is connected with an empty wash-bottle, or a wash-bottle containing concentrated sulphuric acid, the object of which is to prevent any spray from passing over into the salt solution. From the wash-bottle a delivery tube passes which has a funnel fastened at its end by a piece of rubber tubing. The apparatus is so arranged that the funnel dips about 2.5 cm. below

the surface of the salt solution. If from any cause a back pressure is produced, the salt solution will only be driven a few cm. up the funnel, after which air will bubble up. Another advantage in using the funnel is that if a small delivery tube were employed it would soon become choked with solid sodium chloride.

When the solution is saturated with gas, the delivery tube is removed and the beaker set aside for an hour or two. The supernatant liquor is poured off and the sodium chloride transferred to a Buchner funnel which is connected with the vacuum-pump; after the mother-liquor has drained off, it is washed first with a few c.c. of distilled water and then with purified alcohol. It is then spread on a porous porcelain plate to drain, and finally dried in the steam oven.

### Double Salts.

A double salt is a crystalline compound of two or more normal salts with each other. For example, when solutions of ferrous sulphate and ammonium sulphate are mixed together, a crystalline compound containing equal molecules of the iron and the ammonium salt is obtained,  $\text{FeSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ . If the solutions are mixed in molecular proportions, then on concentration the whole of the iron and ammonium salts are obtained as the double compound *Ferrous Ammonium Sulphate*. On the other hand, if the ammonium sulphate is in excess, then sufficient will combine with the ferrous sulphate to form the double salt which will crystallise out, and on further concentration only ammonium sulphate will be obtained. These double salts do not appear to exist in solution as such, at any rate in dilute solution, but they are obtained as solids on crystallisation. Usually the double salts are less soluble in water than their components, hence on mixing strong

solutions of the two substances the double salt readily crystallises out.

The double salts are often used in chemical analysis, because they are readily obtained in a state of purity. Ferrous ammonium sulphate, for example, is not so readily oxidised as ferrous sulphate, and is therefore more readily preserved, and for the same reason it is used for standardising solutions of potassium permanganate. One-seventh of the weight of ferrous ammonium sulphate consists of iron.

#### **Ferrous Ammonium Sulphate.**

Dissolve 35 grm. of crystallised ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , in 60 c.c. hot distilled water to which has been added two or three drops of conc. sulphuric acid. Also dissolve 24 grm. of ammonium sulphate in 30 c.c. hot distilled water. If the solutions are not clear they must be filtered. Now mix the two solutions and stand the beaker containing them in a basin of cold water. Stir until cool and then allow to stand for two hours. The object of proceeding in this manner is to obtain the double salt as a fine granular powder, as it is more readily washed and is more convenient for future use. Now filter on the filter-pump, wash with a little cold water, and then with a little pure methylated spirit. Spread on a porous plate to dry. When, on rubbing with the finger, the crystals no longer adhere together, the substance is quite dry and may be bottled.

#### **Nickel Ammonium Sulphate.**

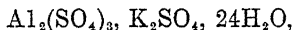
Take 54 grm. crystallised nickel sulphate,  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ , and dissolve in 60 c.c. hot water. Also 25 grm. ammonium sulphate and dissolve in 35 c.c. hot water. Mix the solutions and proceed as above.

### Cobalt Ammonium Sulphate.

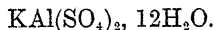
This may be prepared in a similar manner, using equimolecular proportions of the two salts. If it is desired to obtain large crystals, the solutions employed must be more dilute. For this purpose solutions saturated at ordinary temperatures may be employed, and then after mixing allowed to crystallise in a wide open vessel by slow evaporation at ordinary temperature.

### The Alums.

Common alum is a double salt of aluminium sulphate and potassium sulphate, often written as



but it is simpler to express the formula as



The place of potassium may be taken by ammonium, sodium, rubidium, caesium, and also by certain organic derivatives of ammonium. The aluminium can be replaced by other trivalent ions, such as chromium, manganese, iron, etc. It is also possible to replace the sulphanion  $\text{SO}_4''$  by the selenanion  $\text{SeO}_4''$ .

The alums crystallise as octahedra belonging to the regular syetem, and as they are isomorphous with each other, a crystal of one alum can act as a nucleus for crystallisation from a supersaturated solution of another alum. Thus if a large perfect crystal of potash alum is put into a saturated solution of chrome alum, as the solution evaporates the chrome alum will crystallise on the faces of the potash alum. After a few days the crystal may be taken out, and on rubbing down upon a

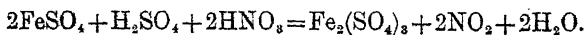
sand-blasted glass plate, the chrome alum can be distinguished laminated upon the potash alum.

### Potash Alum.

Prepare cold saturated solutions in equi-molecular proportions of potassium sulphate,  $K_2SO_4$ , and of aluminium sulphate,  $Al_2(SO_4)_3 \cdot 12H_2O$ . Mix the solutions and allow to stand in a moderately warm place. After a day or two pick out the best-formed crystals, place them in a crystallising dish and pour the mother-liquor over them, repeating this process from day to day until one or two good crystals have been obtained. The temperature of the place should be kept as even as possible, otherwise, if the temperature rise or fall too rapidly, the crystals will not form well, the solution becoming alternately below saturation and supersaturated.

### Iron Ammonium Alum.

1. Dissolve 100 grm. crystallised ferrous sulphate,  $FeSO_4 \cdot 7H_2O$ , in about 180 c.c. boiling water and add 12 c.c. conc. sulphuric acid. Now in order to oxidise the ferrous sulphate into ferric sulphate, add to the boiling solution concentrated nitric acid, a few c.c. at a time. After adding about 15 c.c. of nitric acid, take about 1 c.c. of the solution, dilute to about 10 c.c. and add a few drops of potassium ferricyanide. If no blue precipitate or colouration is produced, then the ferrous salt has been completely oxidised to the ferric condition, and it is unnecessary to add any more nitric acid. The reaction which takes place may be represented thus:—



. As soon as the oxidation is complete, evaporate the solution on the sand-bath to a syrupy consistency and then carry on the evaporation on the water-bath until the mixture becomes almost solid. The reason for concentrating in this manner is to drive off the excess of nitric acid. Dilute with water.

2. Now dissolve 52 grm. of ammonium sulphate in 80 c.c. water. Mix the two cold solutions together and allow to stand overnight, when a large quantity of the iron alum will crystallise out in the form of large straw-coloured or purple octahedra. Since the colour of the ferric ion,  $\text{Fe}^{+++}$ , is a light brown, the purple which is generally a characteristic of the iron alum is supposed to be due to a minute trace of manganese.

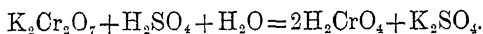
### Potassium Chrome Alum.

Dissolve 3 parts of potassium dichromate in 12 parts of water and then add 4 parts of concentrated sulphuric acid. Allow the mixture to cool, transfer to a porcelain basin and float upon water in which some ice has been placed. Now run in 80 per cent. methylated spirits with constant stirring until the smell of aldehyde gradually disappears. Allow to stand for twenty-four hours. At the end of this time a greyish-violet powder of chrome alum will have settled out. Filter this off on the pump and wash with cold water until it assumes a pure violet colour and the wash water also assumes a violet tinge. Now transfer to a flask and dissolve in as small a quantity of water as possible at a temperature of  $35^{\circ}$ - $40^{\circ}$ . This should be done by placing the flask containing the chrome alum and water in a water-bath heated to a temperature of  $35^{\circ}$ - $40^{\circ}$ . The temperature must not be raised higher than this, otherwise the chrome alum will be decomposed and a sticky, more or

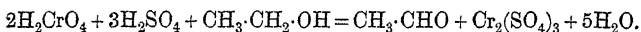
less resinous, mass obtained, which only becomes crystalline after long-continued standing.

After dissolving, stand in a cool place for twenty-four hours, when the chrome alum will have crystallised out. In order that the mixture should not cool too rapidly it is advisable to stand the basin containing it upon a sheet of asbestos and cover it with a clock glass. If it cools too rapidly good crystals are not obtained.

The first reaction on adding the sulphuric acid converts the potassium dichromate into chromic acid and potassium sulphate.



The alcohol then reduces the chromic acid in presence of excess of sulphuric acid to chromic sulphate, being itself oxidised to aldehyde. The chromic sulphate then unites with the potassium sulphate to form potassium chrome alum.



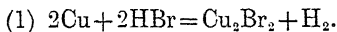
It should be remembered that the alums only exist in the solid state, and that when dissolved in water there are present equal molecules of the constituent sulphates—in the case of ordinary potash alum, for example, potassium and aluminium sulphates. As, however, both of these sulphates are more soluble in water than the alum, the solution becomes supersaturated with respect to the alum before it does with respect to either of the sulphates, and therefore the alum crystallises out.



### Cuprous Chloride.



Copper itself will not dissolve in hydrochloric acid, although it is dissolved by warm hydrobromic acid with evolution of hydrogen. When the reaction is first started, a brownish-coloured solution is produced owing to the admixture of cupric salt. The mixture, however, soon becomes colourless through the reduction of the cupric salt by the hydrogen. The excess of hydrobromic acid causes the formation of unstable *cuprous hydrobromic acid*. On addition of excess of water this is decomposed and white cuprous bromide is precipitated.

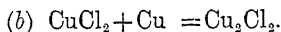
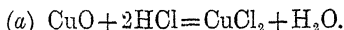


*Cuprous Chloride* can be obtained by dissolving cupric oxide in hydrochloric acid and reducing the cupric chloride thus formed with metallic copper.

Take 10 grm. cupric oxide and warm it with 250 c.c. hydrochloric acid (sp. gr. 1.12) until all the cupric oxide has dissolved. Now add to the dark green solution 20 grm. of clean copper turnings and warm until the solution loses its dark colour and becomes clear and colourless. As soon as the solution is colourless pour it into about one litre of water, taking care that no undissolved copper is poured in with it. Allow the white precipitate to settle, decant off the bulk of the solution, and wash by decantation twice with dilute hydrochloric acid. Now transfer to a Buchner funnel and filter on the vacuum-pump, washing two or three times with water containing a small quantity

of hydrochloric acid, then twice with alcohol, and finally with a small quantity of dry ether. Remove from the filter, spread upon a porous plate and place in an evacuated desiccator over sulphuric acid. In order to completely remove the alcohol and ether, it is advisable to have an evaporating basin in the desiccator containing a little solid paraffin wax.

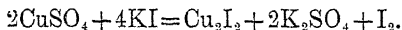
The first reaction which takes place when the cupric oxide is dissolved in the hydrochloric acid is the formation of cupric chloride; this is then reduced by the metallic copper, with formation of cuprous chloride, which in presence of excess of hydrochloric acid remains in solution as cuprous hydrochloric acid,  $\text{H}_4\text{Cu}_2\text{Cl}_6$ . This acid is not known in the free state, but salts such as  $\text{K}_4\text{Cu}_2\text{Cl}_6$  are known. The cuprous chloride is precipitated on pouring the acid solution into water.



### Cuprous Iodide.

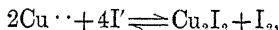


When a soluble iodide is added to a solution of cupric sulphate, cuprous iodide is produced and iodine is liberated thus:—



We may presume that in the first place cupric iodide is produced, but at the moment of its formation it is converted into cuprous iodide and iodine is liberated. The reaction is, however, never quite complete, a certain portion of the

- copper always remaining in solution as cupric ions, an equilibrium being produced.

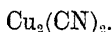


If, however, a third substance is added which will remove one of the reaction products, such as  $\text{SO}_2$  which removes the iodine, the equilibrium balance is destroyed and the reaction completes itself. In fact, the action is now quantitative and is used in analysis for estimating copper gravimetrically.

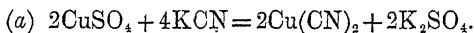
In order to prepare cuprous iodide, dissolve 5 gm. crystallised copper sulphate in about 60 c.c. water, pass in sulphur dioxide or add a strong solution of sulphurous acid until the solution smells strongly of the gas. Then add a solution of 8 gm. potassium iodide in 20 c.c. water and stir up the mixture well. A copious, light, flesh-coloured precipitate will be produced. Allow to stand ten minutes, filter on a Buchner funnel, and wash well with water containing a small quantity of sulphurous acid. Finally spread on a plate and dry in the steam oven.

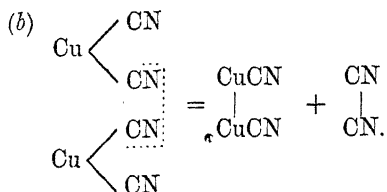
The yield should be quantitative.

### Cuprous Cyanide and Cyanogen.



Cuprous cyanide is prepared in a similar manner to cuprous iodide, *i.e.* by the addition of potassium cyanide to a cupric salt. Presumably at the moment of addition cupric cyanide is produced, but this being unstable immediately changes over into the cuprous condition with liberation of cyanogen. The reaction in this case completes itself, because the gaseous cyanogen produced is immediately removed from the sphere of action.





In preparing cuprous cyanide, one has to be careful not to add an excess of potassium cyanide, because cuprous cyanide is dissolved by it with formation of complex salts. In strong solutions the salt is  $\text{K}_3\text{Cu}(\text{CN})_4$ , in more dilute solutions,  $\text{KCu}_2(\text{CN})_3$ . A solution of cuprous cyanide in potassium cyanide is often employed in copper-plating baths, especially for plating iron or steel where an acid bath is inadmissible; although, after being lightly coated in a cyanide bath the plating is usually completed in an acid bath.

*Preparation.*—To prepare cuprous cyanide take a 5 per cent. solution of copper sulphate and slowly run in a 5 per cent. solution of potassium cyanide until, on allowing the precipitate to settle, the supernatant liquid is only slightly coloured blue. Pour off the bulk of the solution, and finally wash on the vacuum-filter with hot water. The precipitate being rather slimy does not wash very well.

### Cyanogen.

As has already been shown, when potassium cyanide acts upon a solution of cupric sulphate, cyanogen gas is evolved. This fact gives a very convenient method for preparing the compound. Place a warm saturated solution of cupric sulphate into a 500 c.c. flask to which is fitted a dropping funnel and delivery tube (fig. 10). Partially fill the dropping funnel with a 15 per. cent. solution of

potassium cyanide. Gently heat the flask by means of a Bunsen burner and allow the potassium cyanide to run into the copper sulphate solution drop by drop. The mixture will begin to froth and bubbles of gas will rise from the end of the delivery tube. As soon as all the air has been expelled from the apparatus fill a gas jar with cyanogen gas and apply a light. The cyanogen gas will burn with a peach-blossom coloured flame the edges of

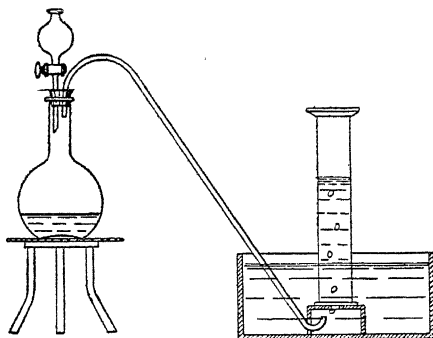
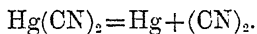


FIG. 10.

which are of a lambent violet. *Be careful not to inhale the gas, as it is very poisonous.*

Cyanogen gas is not quite insoluble in water, the solubility being about the same as that of carbon dioxide. The water therefore takes on the peculiar and unpleasant characteristic odour of the gas.

Another method often employed for preparing the gas is to heat mercuric cyanide in a hard glass tube.



Cyanogen is formed when nitrogen and carbon are brought together at high temperatures, *e.g.* when an electric arc is caused to pass between two carbon rods

enclosed in an atmosphere of nitrogen. It is also found in the gases escaping from the blast-furnaces.

### **Manganous Sulphate.**

(Manganous Ammonium Sulphate.)

Take 30 grm. powdered pyrolusite, place in an evaporating basin, just cover with concentrated sulphuric acid, and heat on a sand-bath in the draught cupboard until the whole of the substance has turned a whitish pink. Continue heating until fumes of sulphuric acid no longer come off, and then heat for another two hours; the last heating may be done over the naked flame or in a muffle furnace, heated to low redness.

The final strong heating is to decompose ferric sulphate and convert it into ferric oxide. Commercial pyrolusite always contains considerable quantities of ferric oxide which is converted into ferric sulphate on warming with sulphuric acid. It is, however, very much less stable than manganous sulphate, and upon heating is decomposed. In fact, if the mixture is sufficiently heated, the whole of the ferric sulphate is decomposed. As this, however, takes some time and requires a certain amount of experience, the following method is advised:—

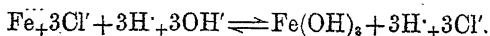
After cooling treat the mixture with excess of water and filter off from any ferric oxide which is precipitated. Transfer to a beaker, add about 10 grm. of barium carbonate, and allow to stand, with occasional stirring, for about four hours, then filter off a few c.c. of the solution and treat it with ammonium sulphide; if a pure flesh-coloured precipitate, completely soluble in acetic acid, is produced, the manganous sulphate is free from iron and may be evaporated to crystallisation. Or the iron may be tested for with ammonium thiocyanate. If iron is still present,

the solution must be allowed to stand for a further period over the barium carbonate.

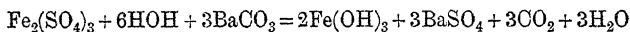
Evaporate the solution to crystallisation and stand in a cool place overnight. If the crystals come out in a powdery form, add just sufficient water to dissolve them when the temperature is raised to 30° and then allow to stand for a few days. In this way fairly large crystals of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  are obtained.

As, however, manganous sulphate is rather difficult to obtain in the form of good crystals, **manganous ammonium sulphate**,  $\text{MnSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , may be prepared. Evaporate the solution of manganous sulphate down until, on cooling, crystals just commence to separate out. Add *just* sufficient water to dissolve these and measure the volume of the solution. Now at 20° 100 parts of water will dissolve 30 parts of  $\text{MnSO}_4$ . Therefore, knowing the quantity of manganous sulphate which you have, it is easy to calculate the amount of ammonium sulphate required to produce the mixed salt. Prepare a nearly hot saturated solution with the requisite quantity of ammonium sulphate, and add it to the hot solution of the manganous sulphate. Stand the mixture in a basin of cold water and stir until cold. Allow to stand for half an hour and filter off, wash with cold water, and dry on a porous plate.

The separation of iron from manganese by the above method depends upon the fact that the trivalent metals, iron, aluminium and chromic salts, are precipitated in the cold by barium carbonate as hydroxides, but the divalent metals, manganese, zinc, cobalt, and nickel, are not; they are, however, to a certain extent on boiling. The action is caused by the greater hydrolysis of the trivalent metals. Thus in solution ferric chloride is strongly hydrolysed.



We have therefore in solution colloidal ferric hydroxide and free acid. If the free acid is removed by the addition of barium carbonate, equilibrium is disturbed and hydrolysis is carried further until finally the insoluble ferric hydroxide is precipitated out (see colloidal solutions, p. 141). The rôle of the barium carbonate is simply to neutralise the free acid and so to cause complete hydrolysis, thus:—



### Manganous Chloride.

(From residues obtained in the preparation of Chlorine.)

Chlorine gas is usually prepared in the laboratory by acting upon *pyrolusite* with concentrated hydrochloric acid. But as has already been stated (see manganous sulphate, p. 44) *pyrolusite* contains oxides of iron as well as of manganese, therefore the manganous chloride obtained is always more or less contaminated with ferric chloride, and on crystallisation has a dirty brown tinge.

In order to purify the manganese chloride, filter from any residue and evaporate the solution to dryness on the sand-bath in a draught cupboard. Now heat for about two hours on a wire gauze, breaking up the mass so that all parts become equally heated. The heating decomposes the ferric chloride but has little action on the manganous chloride. Treat the cooled mass with several small portions of hot water and filter from sediment.

The above treatment never completely eliminates the iron, and therefore further treatment is necessary. The iron could readily be removed by the method employed to remove it from manganous sulphide, but in this case soluble barium chloride would be produced which would

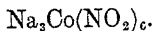


contaminate the manganous chloride. The following method should therefore be employed :—

Measure the volume of solution and take  $\frac{1}{12}$  of it. Treat this with an excess of sodium carbonate, allow the precipitate of manganous carbonate to settle, and wash it three or four times by decantation with hot water. When the precipitate has been washed, mix it with the main portion of the manganese solution. Digest on a water-bath until a small portion of the filtered solution gives a pure flesh-coloured precipitate when treated with ammonium sulphide, and which dissolves in acetic acid without residue. Filter off from the residue and evaporate on the water-bath until crystals commence to form on the surface of the liquid while it is still hot.

Manganous chloride crystallises in light pink monoclinic tablets containing  $4\text{H}_2\text{O}$ . The anhydrous salt can only be obtained by heating the crystallised salt in a stream of dry hydrochloric acid gas. Or by conducting a stream of dry hydrochloric acid gas over heated dry manganous carbonate.

### Sodium Cobaltinitrite.



Dissolve 150 grm. of sodium nitrite in 150 c.c. of hot water. Cool the solution to  $50^\circ$  and add to it 50 grm. of crystallised cobalt nitrate. As soon as all the cobalt nitrate has dissolved add 25 c.c. of glacial acetic acid. Mix the solution well, allow to stand for twenty minutes, and filter off from any *potassium* cobaltinitrite which may have been formed owing to traces of potassium nitrate in the sodium nitrate. Now aspirate a current of air through the filtrate for half an hour to remove oxides of nitrogen. The simplest way to aspirate air through the solution is to

take an ordinary filter-flask, the neck of which is closed with a cork, through which a glass tube reaching nearly to the bottom of the flask is passed. The tubulus is connected with a vacuum-pump (fig. 11).

Now add 150 c.c. of alcohol, allow the mixture to stand for an hour, with occasional shaking, and filter on the vacuum-pump. Wash two or three times with small quantities of alcohol and spread upon a porous plate until dry.

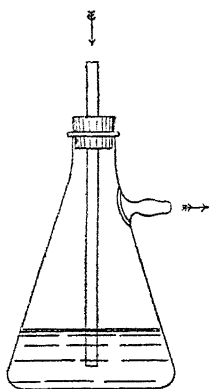
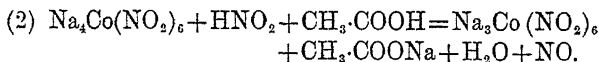
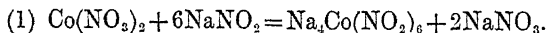
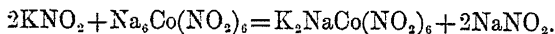


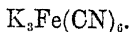
FIG. 11.

The reaction probably takes place in two stages. When the cobalt nitrate or chloride is brought into contact with the sodium nitrate, sodium cobaltonitrite is produced, which is then oxidised to the cobaltinitrite by the nitrous acid liberated from the excess of the sodium nitrite on the addition of acetic acid. This reaction is analogous to the oxidation of potassium ferrocyanide to potassium ferricyanide by the action of chlorine.

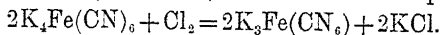
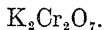


The sodium cobaltinitrite so obtained is a more or less crystalline orange powder. It is employed as a test for the potasium and ammonium as the salts of these cations with the cobaltinitrite anion are very sparingly soluble in water. The insoluble salt, however, is a dipotassium or diammonium sodium cobaltinitrite.



**Potassium Ferricyanide.**

Dissolve potassium ferrocyanide in water and pass chlorine gas into the cold solution until it no longer gives a precipitate with ferric chloride. Excess of chlorine should not be passed, because this forms Prussian green. Evaporate to crystallisation and filter hot from a blue precipitate which is invariably produced. The substance will probably require to be recrystallised in order to obtain it pure.

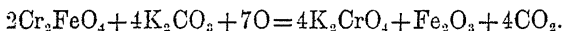
**Potassium Dichromate.**

Take 100 grm. powdered chrome iron ore ( $\text{Cr}_2\text{FeO}_4$ ) and mix in an iron crucible with 200 grm. potassium carbonate, and 20 grm. potassium nitrate. The crucible should not be more than about two-thirds filled, otherwise on fusing the mixture will bubble over, some of it be lost, and the floor of the furnace made in a mess.

Now heat over the blowpipe or in the furnace until the whole mass is thoroughly fused and bubbles of gas are no more given off. Pour the fused mass upon a cold iron plate, *e.g.* a sand-bath. When cold, powder roughly in a mortar and boil up with two or three quantities of water until no more is dissolved, and filter from the undissolved iron salts.

I. If it is desired to prepare potassium chromate, slightly acidify the solution with acetic acid, boil and filter. This will precipitate any silica and aluminium oxide which might be present: now neutralise with potassium carbonate. On evaporating down, yellow crystals of potassium chromate separate out, which should be purified by recrystallisation.

II. To prepare **potassium dichromate** render the solution, of the chromate, just acid with sulphuric acid, boil and filter. The potassium dichromate crystallises out on concentrating. If necessary it can be purified by recrystallisation.



Commercially, the chrome iron ore is very often ignited with chalk and the calcium chromate thus produced is decomposed by adding a hot solution of potassium sulphate.

**SOLUBILITIES OF POTASSIUM CHROMATE AND DICHROMATE.**  
Parts per 100 parts of water.

| Temperature. | Potassium Chromate. | Potassium Dichromate. |
|--------------|---------------------|-----------------------|
| 0°           | 58.90               | 4.60                  |
| 10°          | 60.92               | 7.40                  |
| 20°          | 62.94               | 12.40                 |
| 30°          | 64.95               | 18.40                 |
| 40°          | 66.98               | 25.90                 |
| 50°          | 69.00               | 35.00                 |
| 60°          | 71.02               | 45.00                 |
| 80°          | 77.06               | 68.60                 |
| 100°         | 79.10               | 94.10                 |

**Potassium Permanganate.**



Mix 2 parts of potassium hydroxide with 1 part of potassium chlorate in a sheet-iron or nickel crucible and heat over the Bunsen burner until the mixture becomes

fluid. Now remove the burner and gradually stir in with an iron spatula 2 parts of finely powdered manganese dioxide (pyrolusite). The addition of pyrolusite must be made cautiously, otherwise the reaction may be violent. Now heat to dull redness, at the same time stirring about and breaking up the lumps with the iron spatula until the product is hard and appears quite dry. Place the crucible while still warm into cold water, and then, when the mass has been removed from the crucible, grind up in a mortar with water. Too much water should not be added (about 40 c.c. water to every grm. of potassium chlorate taken). Transfer the muddy fluid to a flask and boil on the sand-bath, at the same time passing a rapid stream of carbon dioxide through the liquid. This is to be continued until, upon letting a drop of the solution fall on filter-paper, a purple stain is produced, the edges of which have no green appearance.

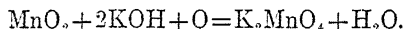
Now cool the mixture and allow to stand until the hydrated oxide of manganese has settled, and carefully decant through an asbestos filter. Evaporate the solution until a drop of it taken out and placed upon a watch-glass almost immediately forms crystals. On allowing to stand overnight, the main portion of the potassium permanganate will have crystallised out. It is best to separate it from the mother-liquor by decantation, after which it may be washed with a small quantity of cold water and air-dried on a porous plate. The yield is about 12-15 grm. for every 50 grm. of manganese dioxide taken. If necessary, the product may be purified by recrystallisation. When it is to be used for analysis it is always advisable to recrystallise the salt.

*Reaction.*—When manganese dioxide is fused with caustic potash and potassium chlorate, potassium manganate is produced. If fused in absence of potassium chlorate only

one-third of the manganese dioxide is converted into the manganate, two-thirds being reduced to manganese sesquioxide, thus:—



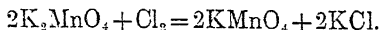
But in presence of potassium chlorate or other oxidising agent, such as potassium nitrate, the oxidation is complete, thus:—



At this stage there are always considerable quantities of impurities, such as ferric oxide, which arise from impurities in the original pyrolusite. It is not, however, necessary to separate them until the manganate has been converted into permanganate by passing in carbon dioxide.



Chlorine may be used instead of carbon dioxide, in which case, however, it is better to filter off any impurities left after the fusion before passing in the chlorine, and then the solution of potassium permanganate may be evaporated to crystallisation without requiring to be first filtered.



### Sodium Nitrite.

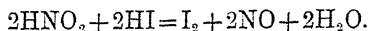


Melt 85 grm. sodium nitrate in a clean new sand-bath and add, in small quantities at a time, with constant stirring, 200 grm. granulated lead. After all the lead has been added continue heating and stirring until the whole of the lead has become oxidised, generally from forty-five minutes to one hour. As soon as this has taken place pour

the fused mass upon a cold iron plate. When cool, powder the solid cake in a mortar and lixivate several times with small quantities of boiling water. This may very well be done by placing on a funnel which has been plugged with a little asbestos, and then spray on boiling water from a wash-bottle.



Pass a rapid stream of carbon dioxide through the filtrate, to remove any soluble lead salt, for five or ten minutes; boil and filter. Now evaporate down the solution until, on taking out a drop of the solution and placing it upon a watch-glass, crystals begin to separate; these are mainly unchanged sodium nitrate. Allow to cool and pour off the solution from the crystals. Wash the crystals with a small quantity of cold water and add the washings to the original solution. Repeat the operation of evaporation and crystallisation until the solid, after washing, shows a distinct test for nitrites. The best test to apply is to acidify the solution with dilute sulphuric acid, then to add a solution of potassium iodide and starch paste; if a distinct blue colouration is produced, then sodium nitrite is present in the solid substance.



Now evaporate the mother-liquor to dryness and extract three to four times with boiling absolute alcohol.

The extraction can be more thoroughly and easily carried out by using a Soxhlet extracting apparatus (fig. 12). The substance to be extracted is placed in the extraction tube, A, a little glass wool being

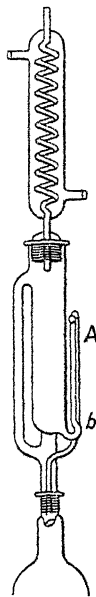
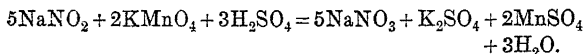


FIG. 12.

first placed on the bottom of the extractor to prevent the powdered substance from blocking the siphon tube, *b*. Alcohol is placed in the flask and caused to boil by placing the flask on a water-bath; the vapour then passes up into the extractor and is condensed by the condenser fixed into the top of the extractor. As soon as the condensed alcohol reaches to the top of the siphon tube, the siphon acts, and the alcohol containing dissolved sodium nitrite flows back into the flask. The apparatus acts automatically, and in the course of an hour or so all the sodium nitrite has been extracted and only sodium nitrate remains in the Soxhlet. When the sodium nitrite is extracted in this manner it is only necessary to separate the first portion of sodium nitrate, after which the whole solution may be evaporated to dryness.

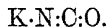
Distil off the alcohol and recrystallise the sodium nitrite from a small quantity of water.

Dry the crystals on a porous plate, weigh them, and calculate the yield of pure sodium nitrite by titrating with potassium permanganate.



In order to carry out this estimation, dissolve about 0.5 grm. of the nitrite in 400 c.c. water, then add a considerable excess of dilute sulphuric acid and titrate with  $\frac{\text{N}}{10}$   $\text{KMnO}_4$ .

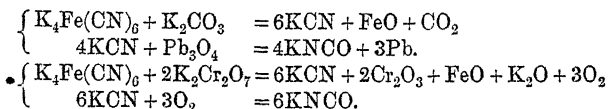
### Potassium Isocyanate.



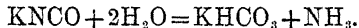
When potassium cyanide is oxidised either by long-continued melting in the air, or, better, by melting in presence of an oxidising agent such as a metallic oxide or potassium



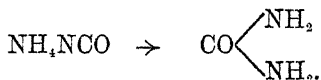
dichromate, it is converted into potassium isocyanate. It can also be obtained by heating a mixture of potassium carbonate and potassium ferrocyanide with red lead, or by heating potassium ferrocyanide with potassium dichromate alone. In the two latter cases, however, the first product of the reaction will be the formation of potassium cyanide, which is then oxidised by the oxygen from the red lead or the potassium dichromate.



Although the potassium isocyanate is readily formed, it is by no means an easy matter to obtain it in the pure state, owing to its instability. When boiled with water, or even on standing in contact with cold water, it is hydrolysed into potassium bicarbonate and ammonia.



It is not possible to prepare the ammonium salt in the solid state, because on warming the solution an intermolecular change takes place, and it passes over into urea.

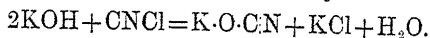


*Preparation.*—Roughly powder 110 gm. potassium ferrocyanide, spread it out thinly upon an iron plate, and heat it with a Bunsen burner, keeping the flame of the burner about 3 cm. away from the iron. Continue the heating until the powder is quite white, then grind up finely in a mortar, and again heat for about an hour. It is important that the salt should be absolutely free from moisture. Now mix while still warm with 75 gm.

powdered potassium dichromate which has been previously fused in a porcelain basin and poured out upon a cold iron plate. Place the mixture into an iron crucible, and heat strongly over the Bunsen burner until the whole mixture is black and semi-fluid. While still semi-fluid, scrape out from the crucible and grind up warm in a mortar. Place the powdered substance in a flask, and pour on to it a mixture of 450 c.c. 80 per cent. alcohol and 50 c.c. methyl alcohol. Put the flask in a boiling-water bath, and shake continually for ten minutes. Now filter into a beaker which is standing in ice water. Also, as soon as the whole of the liquid has been poured off from the residue in the flask, cool the flask with ice water. When the solution in the beaker is quite cold, pour off from the crystallised cyanate, and use the mother-liquor for a further extraction, proceeding as before. The extraction should be repeated four times, and the solution obtained from each extraction filtered into a different beaker. At the end the different portions of the cyanate are placed upon a Buchner funnel and washed on the funnel with ether, finally dried in a vacuum desiccator over sulphuric acid. About 30 grm. of pure product should be obtained. The operation of crystallisation should be performed as rapidly as possible.

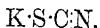
*Preparation of Urea from the Mother-liquors.*—There is still a considerable quantity of potassium cyanate in the mother-liquors, but this cannot be obtained by distilling off the alcohol, because it is thereby decomposed. In order to convert this into urea, dissolve 35 grm. ammonium sulphate in 50 c.c. water, and add this solution to the alcoholic solution. Now distil off the alcohol, evaporate the residue to dryness, and extract the urea with 95 per cent. alcohol. The extraction may very readily be carried out in a Soxhlet (p. 53).

**Potassium Cyanate**,  $\text{K}\cdot\text{O}\cdot\text{C}\cdot\text{N}$ , can be prepared by passing cyanogen chloride into potassium hydroxide solution,



It is, however, very unstable.

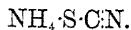
### **Potassium Thiocyanate.**



Whereas the ordinary modification of potassium cyanate is the isocyanate, the stable sulphur compound is the true thiocyanate. It is readily prepared by adding sulphur to melted potassium cyanide, or to a mixture of potassium ferrocyanide and potassium carbonate. Commercially, it is usually prepared from potassium ferrocyanide.

*Preparation.*—Melt 20 grm. potassium cyanide in a porcelain basin, and when melted, remove the flame. Then stir in, in small quantities at a time, 10 grms. of sulphur. The sulphur immediately dissolves in the cyanide, and the mixture becomes light yellow. When all the sulphur has been added, allow to cool, dissolve in hot water, filter, and then evaporate until the surface becomes coated with crystals. Cool and allow to stand overnight, filter on the pump, and purify by recrystallisation.

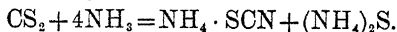
### **Ammonium Thiocyanate.**



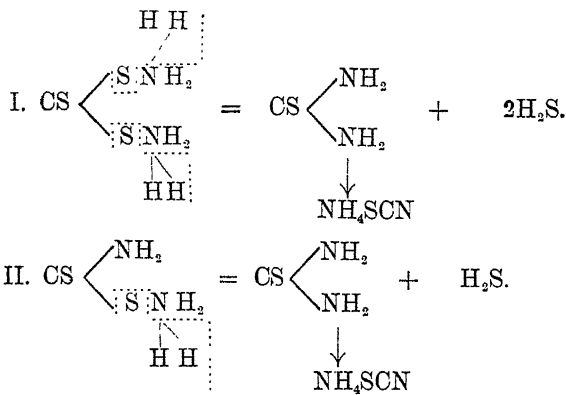
Measure out 100 c.c. carbon disulphide (130 grm.) and place it in a 1-litre flask. Now measure out 300 c.c. ammonium hydrate, sp. gr. 0.912 (4 parts strong ammonium hydrate 0.88 and 1 part water), and 230 c.c. of 95 per cent. alcohol. Mix the alcohol and ammonia with the carbon disulphide and cork the flask. Now set aside in a

moderately warm place and allow to stand for a week with occasional shaking. At the end of this time most of the carbon disulphide will have disappeared. Distil off, in the draught cupboard, two-thirds of the liquid, and filter hot. Evaporate down on the water-bath until a crystalline scum commences to form, and set aside to crystallise. The contents of the evaporating basin should become semi-solid, break up with a bone spatula and filter on the vacuum-pump. Wash with about 20 c.c. of strong alcohol, and when thoroughly drained, spread on a porous plate. The salt will probably be slightly yellow, but on recrystallisation can be obtained quite white. Yield: between 50 and 60 gm.

The reaction may be written



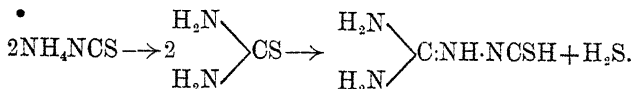
It really, however, takes place in two stages, ammonium thiocarbonate and thiocarbamate being first produced, and these on heating split up into sulphuretted hydrogen and thiourea, which latter by intramolecular change is converted into ammonium thiocyanate.



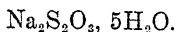
The reaction being the reverse of that which takes place when urea is produced by heating ammonium cyanate.



But when dry ammonium cyanate is heated to a temperature of  $190^\circ\text{--}200^\circ$  it is converted first into thiourea and then the thiourea is changed to guanidine thiocyanate.



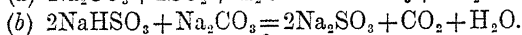
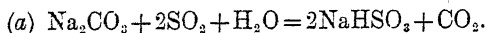
### Sodium Thiosulphate.



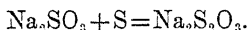
Prepare two saturated solutions of sodium carbonate, each containing 100 grm. of the anhydrous salt. Through one of the solutions pass sulphur dioxide until it is saturated with the gas, that is, until no more gas is absorbed. As soon as the solution is saturated mix it with the other solution. By this means a solution of normal sodium sulphite has been prepared. Now add flowers of sulphur in small quantities at a time to the boiling solution, continuing the addition of the flowers of sulphur until no more is dissolved. Filter the solution to remove excess of sulphur, evaporate to about one-quarter its bulk and set aside to crystallise. It is advisable to purify the product by recrystallisation.

*Reaction.*—When the sulphur dioxide is passed to saturation into the solution of sodium carbonate, sodium hydrogen sulphite is produced, and on adding this to the second

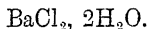
portion of sodium carbonate, the normal sulphite is formed.



The sodium sulphite, on boiling up with sulphur, is then converted into sodium thiosulphate, thus:—



### Barium Chloride.



(From Heavy Spar.)

Heavy Spar or *Barite* consists of crude barium sulphate; from it or the carbonate *Witherite* most barium compounds are obtained.

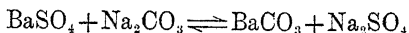
Take 50 grm. powdered barite and mix it with 100 grm. fusion mixture (a mixture of molecular proportions of potassium and sodium carbonates). Place the mixture in a Cornish crucible so that the crucible is about two-thirds full.<sup>1</sup> Put in a muffle or crucible furnace and heat to a full red heat until the mixture is completely fused and forms a thin fluid. Remove the crucible from the furnace and pour the fused mass upon an iron plate.

When cool, break up the solid cake and powder it in a mortar. Mix the powdered substance, which consists of barium carbonate and sodium and potassium sulphate with a medium quantity of hot water, and filter. Wash on the filter first with a hot solution of sodium carbonate and then with hot water until the filtrate no longer gives a test for sulphates.

<sup>1</sup> If the crucible is filled with the mixture, on heating, when the reaction commences, the contents boil over and cause loss, besides spoiling the bed of the furnace.

Now dissolve the barium carbonate in 4N. hydrochloric acid. If a clear solution is not obtained, filter, and then evaporate to crystallisation; set aside overnight to crystallise.

The conversion of barium sulphate to the carbonate is a good example of Mass Action. When barium sulphate is heated with an excess of a solution of sodium carbonate it is partially converted into the carbonate. Unless, however, the

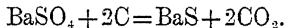


concentration of the sodium carbonate is very great the reaction is not complete because, as is shown in the equation, sodium sulphate can also convert barium carbonate into the sulphate. The greatest concentration of sodium carbonate is obtained by fusing it in contact with barium sulphate, then the reaction from left to right is quantitative.

### Barium Monoxide.



Heavy spar may be converted into barium carbonate as described on page 60, and then treated with nitric acid to convert the carbonate into barium nitrate. Or the heavy spar may be reduced to barium sulphide by igniting with powdered charcoal, thus:—



In order to do this take 1000 grm. powdered heavy spar and thoroughly mix with 300 grm. powdered wood charcoal. Place in a fireclay crucible, cover with a layer of charcoal, and heat in the furnace to bright redness for from 2 to 2½ hours.

Allow to cool, throw into about one litre of water, then cautiously add dilute nitric acid (1 : 3) until the solution is just acid. This operation is best carried out in the draught cupboard owing to the evolution of sulphuretted hydrogen. Heat the solution to boiling and filter hot. Then evaporate to crystallisation, allow to stand for twenty-four hours, and filter off the crystals of barium nitrate. Dry on a porous plate, and finally at 100°. When dry, powder the crystals finely and mix with powdered charcoal; for every 100 grm. of barium nitrate add about 18 grm. of charcoal. Place the mixture on a clean sand-bath and heat strongly. As soon as reaction has commenced it is not usually necessary to heat further, as when once started the reaction will continue until the whole of the barium nitrate has been decomposed. If charcoal is not added to the barium nitrate it is necessary to heat to a very high temperature in order to cause it to decompose. When this is done in a crucible it is afterwards difficult to get the oxide out of it. In the reaction with carbon the whole of it gets oxidised to carbon dioxide. When cool, break the oxide off the sand-bath, place it in a crucible, and heat it in the furnace to full redness; if this is not done, there is usually a little undecomposed nitrate left in the ignited mass. The oxide must be kept in a well-stoppered bottle, as it rapidly takes up moisture and carbon dioxide from the air.

### Barium Peroxide.



When barium monoxide is heated in a current of air or oxygen it takes up an atom of oxygen, and is converted into the peroxide. When this barium peroxide is strongly



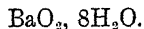
heated it gives up the extra atom of oxygen, so that the reaction is a reversible one,



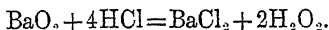
The fact that barium monoxide takes up oxygen at a certain temperature, and again yields it up, either by raising the temperature or by decreasing the pressure, the temperature being kept constant, is made use of in the commercial production of oxygen (Brinn's process).

In order to prepare barium peroxide, fill a combustion tube with barium monoxide, heat to dull redness, and pass oxygen gas over the mass until no more is absorbed. Air may be used instead of oxygen, but in this case the formation of the peroxide takes appreciably longer. The oxygen and air must be free from carbon dioxide. When the process is completed cool the product, and preserve in a well-stoppered bottle.

### Hydrated Barium Peroxide.

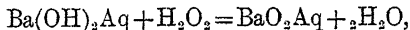


Powder 59 barium peroxide obtained in the last experiment and grind it up into a thin paste with water which has been cooled to  $0^\circ$ . Slowly pour this paste into 600 c.c. ice-cold 2N. hydrochloric acid,



If the solution so obtained is not clear, allow to settle, and decant into a clean beaker.

Now pour into this solution, which should be kept at  $0^\circ$ , a saturated solution of barium hydroxide,



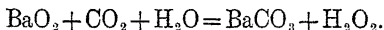
also at  $0^\circ$ , until a perfectly white precipitate is formed, and on further addition of the hydroxide no further pre-

precipitate is produced. Filter off on the vacuum-pump, wash with a little ice-cold water, and preserve in the form of a paste, or else drain on a porous plate, and preserve in a damp condition. The product loses its water on heating to 130°.

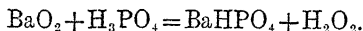
### Hydrogen Peroxide.



Barium peroxide may be decomposed in a variety of ways in order to prepare hydrogen peroxide. Thus a dilute solution can be obtained by suspending the powdered peroxide in water and passing in carbon dioxide.



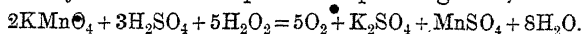
Commercially, hydrogen peroxide is usually obtained by decomposing barium peroxide with phosphoric acid,



Suspend 100 grm. barium peroxide in 100 c.c. water. Cool to 0°, and gradually add, with constant stirring, a moderately strong solution of phosphoric acid, until the solution is *just* acid. Filter off the precipitated barium hydrogen phosphate, and to the filtrate add a paste of barium peroxide (hydrated barium peroxide) until the solution is barely acid; it *must* not be alkaline. Allow to stand in a cold place for twenty-four hours, filter and evaporate on the water-bath in a clean smooth porcelain basin until decomposition just sets in. The decomposition is made manifest by effervescence taking place. In order to concentrate further, distil off the water in vacuo. It is not possible to obtain 100 per cent. solution in this way, because as the hydrogen peroxide becomes stronger it gradually acts upon the glass distilling flask. Final con-

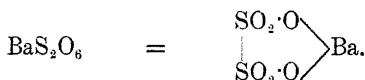
centration must be carried out in a platinum basin, which is placed in an evacuated desiccator over sulphuric acid.

The strength of the hydrogen peroxide may be determined by titration with potassium permanganate, thus:—



Commercially, hydrogen peroxide is sold as of so many volumes strength. This means, for example, that a five-volume solution will give on decomposition with potassium permanganate five volumes of oxygen, and a twenty-volume solution twenty volumes of oxygen. Therefore the strength of the hydrogen peroxide can be, and often is, estimated by measuring the volume of oxygen which is given off when a known volume of the solution is treated with potassium permanganate.

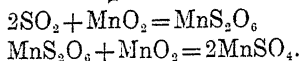
### Barium Dithionate.



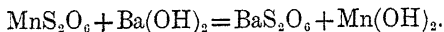
Suspend 50 grm. finely powdered pyrolusite in 250 c.c. distilled water, place in a basin of cold water, and pass in gaseous sulphur dioxide with frequent shaking until the mixture smells strongly. Filter from ferric and manganic oxides. Now add a concentrated solution of barium hydroxide until the solution is just alkaline. Filter from precipitated barium sulphate, and evaporate on the water-bath to crystallisation. On cooling, barium dithionate,  $\text{BaS}_2\text{O}_6 \cdot 2\text{H}_2\text{O}$ , separates out. A solution of the free acid can be obtained by careful decomposition of the barium salt with sulphuric acid, and after decanting from the barium sulphate, concentrating in vacuum.

The concentrated solution has a sp. gr. of 1.347; further concentration causes decomposition.

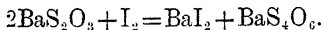
When sulphur dioxide acts upon manganese peroxide suspended in water, manganese dithionate is produced, but a portion of this dithionate reacts with part of the manganese peroxide to produce manganous sulphate,



The addition of barium hydroxide then removes the manganese sulphate and forms with the manganese dithionate, barium dithionate,



**Barium Tetrathionate**,  $\text{BaS}_4\text{O}_{10}$ , can be prepared by acting upon barium thiosulphate with iodine,



It is, however, very unstable. In order to prepare it, suspend 20 grm. barium thiosulphate in a small quantity of cold water, add powdered iodine in small quantities until the mixture assumes a permanent brown colour. Extract the semi-solid mass with alcohol, which dissolves the  $\text{BaI}_2$  and the excess of iodine. The  $\text{BaS}_4\text{O}_{10}$  is obtained on filtering; it is difficult to purify by recrystallisation, as it decomposes on warming with water.

**Barium Thiosulphate** is prepared by adding an excess of a soluble barium salt to a solution of sodium thiosulphate. The precipitated barium thiosulphate is filtered off, washed with a little cold water, and dried on a porous plate.

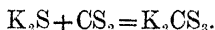
### Potassium Thiocarbonate.



Potassium thiocarbonate is the sulphur compound which

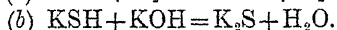
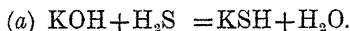
corresponds to potassium carbonate, the oxygen being replaced by sulphur. It may be prepared as follows:—

Dissolve 22 gm. potassium sulphide,  $K_2S$ , in 150 c.c. of water, and add to this solution 15 gm. carbon disulphide. Allow the mixture to stand for twenty-four hours, with occasional shaking, and then warm on the water-bath under a reflux condenser for an hour. On cooling, the potassium thiocarbonate separates out as a white crystalline powder. Filter off and dry on a porous plate.

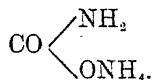


The reaction proceeds better when freshly prepared potassium sulphide is employed. In order to prepare this, take 25 gm. of potassium hydroxide and dissolve it in 100 c.c. water. Divide the solution into two equal portions, saturate the one portion with sulphuretted hydrogen. When saturated, mix the two solutions, and make up to 150 c.c. with distilled water, then proceed as above.

When a solution of potassium hydroxide is saturated with sulphuretted hydrogen, potassium hydrosulphide is formed, and this is converted into the normal sulphide on addition of the potassium hydroxide.

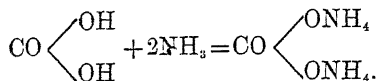


### Ammonium Carbamate.

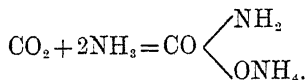
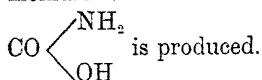


By replacing the OH groups in carbonic acid with ammonia, ammonium hydrocarbonate and ammonium

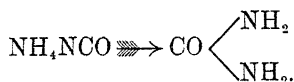
carbonate are produced, the reaction taking place when carbon dioxide is passed into aqueous ammonia.



But by passing dry ammonia gas and dry carbon dioxide simultaneously into absolute alcohol, the ammonium salt of *carbamic acid*, or amido carbonic acid,



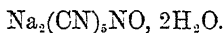
Diamido carbonic acid, or urea (see p. 56), is prepared by simply heating ammonium cyanate, when rearrangement of the molecule takes place, thus:—



*Preparation.*—In order to prepare ammonium carbamate, take 100 c.c. absolute alcohol and pass in dry ammonia and carbon dioxide gas, as far as possible at the same speed. The vessel containing the alcohol should stand in cold water. In a short time the solid carbamate commences to crystallise out, and ultimately the whole liquid becomes thick with minute crystals. Owing to the separating out of the crystals while the gases are passing into the alcohol, the delivery tubes should be wide in order to prevent them becoming stopped up. Allow to stand for about an hour, and filter off on the vacuum-pump. Finally spread upon a porous plate and air dry.

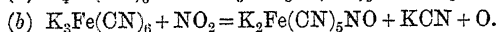
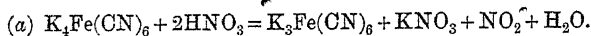
Commercial ammonium carbonate invariably contains ammonium carbamate mixed with it.

### Sodium Nitroprusside.



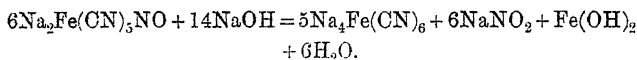
Finely powder 55 grm. potassium ferrocyanide, place it in a flask, and then add an equal weight of conc. nitric acid which has been diluted with its own bulk of water. Shake the flask so as to obtain a homogeneous mixture, heat on the sand-bath, until a drop withdrawn with a glass rod gives no precipitation with ferrous sulphate, showing that all the potassium ferrocyanide has been oxidised. When this result is reached, boil for about five minutes, remove from the sand-bath, and make slightly alkaline with sodium hydroxide. Allow to stand until cold, and filter off the precipitated ferric oxide and crystallised potassium nitrate; the filtration should be done on the pump. Wash the residue with 60 per cent. alcohol. Now evaporate the mixed filtrate to about half its bulk on the water-bath. On cooling, a further quantity of potassium nitrate will separate out; filter. Wash the crystals with two or three small quantities of hot 80 per cent. alcohol. On evaporating the mixed filtrates to about one-third the bulk and allowing to stand overnight, the bulk of the sodium nitroprusside will separate out as ruby-coloured prisms. It will still, however, be more or less contaminated with potassium nitrate, from which it can be separated by digestion with 80 per cent. alcohol, in which the potassium nitrate is only very sparingly soluble. Allow the alcoholic solution to stand for an hour or two, and pour off from any potassium nitrate which may have crystallised out. Finally evaporate to small bulk, when the nitroprusside will separate out in the pure state.

When the nitric acid is added to the potassium ferrocyanide, it first oxidises it to potassium ferricyanide, and nitrogen peroxide is given off, which then reacts with the ferricyanide to form the nitroprusside.



As, however, there is excess of acid present, the acid hydrogen nitroprusside ( $\text{H}_2\text{Fe}(\text{CN})_5\text{NO}$ ) is present, which, on neutralisation with sodium hydroxide, is converted into the sodium salt. The reaction above is not, however, quantitative, because to a certain extent complete decomposition of the ferricyanide takes place, and ferric oxide is produced.

*Properties.*—Sodium nitroprusside forms ruby-red monoclinic prisms, containing  $2\text{H}_2\text{O}$  of crystallisation, which are soluble at ordinary temperatures in 2.5 parts of water. The water of crystallisation is not lost at  $100^\circ$ . The solution gradually decomposes, and a blue precipitate is produced. In alkaline solution it gives an intensive purple, or purple blue colouration, with sulphides, and is thus used as a very delicate test for soluble sulphides. It is decomposed by alkalis as follows:—





## CHAPTER IV

### HALOGENS AND HALOGEN COMPOUNDS

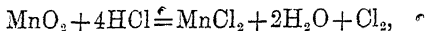
WHEN an element forms more than one halogen compound, the lower one can generally be prepared by the action of hydrochloric acid or by hydrochloric acid gas; whereas by the action of chlorine ether at ordinary temperature, or on heating, the compound containing the greatest number of chlorine atoms is obtained. Thus, when antimony is acted upon with chlorine, antimony pentachloride is formed, whereas, when it is acted upon with hydrochloric acid, the trichloride is produced. Similarly with tin, chlorine produces the tetrachloride, but hydrochloric acid forms the dichloride.

The action of chlorine may, however, be additive, as, for example, with phosphorus, the trichloride is first produced, and then the pentachloride; the same also applies to sulphur, the monochloride is first produced; in this case, however, it is probably due to the instability of the higher chlorides.

#### Chlorine.

As in some of the preparations considerable quantities of chlorine are required, the preparation of the gas by a method which permits of obtaining it in fairly large

quantities is here given.<sup>1</sup> The most satisfactory method, to obtain chlorine in the laboratory is by the oxidation of hydrochloric acid with manganese dioxide (pyrolusite). According to the equation



87 grm. of manganese dioxide requires 146 grm. of gaseous hydrochloric acid to produce 71 grm. of chlorine gas, or taking the strength of concentrated aqueous hydrochloric acid as 33 per cent., 440 grm. of the aqueous acid will be required; in practice considerably more than this is necessary.

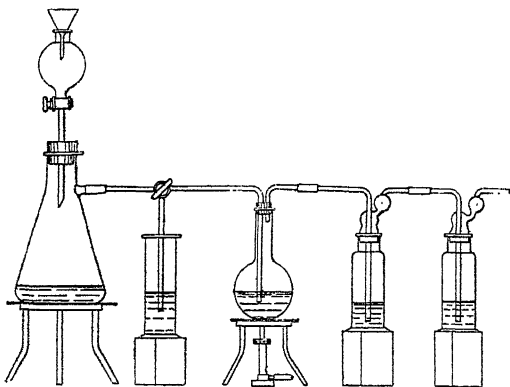


FIG. 13.

In the apparatus illustrated in fig. 13, one-half kilo. of pyrolusite may be taken at one time. This quantity of pyrolusite would require more than 2.5 kilos. of conc. aqueous

<sup>1</sup> When chlorine is required in fairly large quantities, the best method is to obtain it in the liquid form in steel cylinders. Cylinders of liquid chlorine can be obtained from the SCOTCH AND IRISH OXYGEN Co., POLMADIE, GLASGOW.

hydrochloric acid for its complete decomposition. Such a large quantity of acid would necessitate the employment of a very large flask; furthermore, when the reaction has proceeded a certain way, the large amount of water which is formed causes the action to become very slow.

In order to obviate the above difficulties, 500 grm. of granular pyrolusite is placed in a 2-litre flask, together with 1 litre of concentrated hydrochloric acid. The generating flask is fitted with a double perforated rubber stopper. Through one hole a glass tube passes to the bottom of the flask, and is connected with an apparatus for generating hydrochloric acid gas, B, of the same form as that described on p. 32. Between the chlorine generating flask and the hydrochloric acid apparatus is a two-way tap, so that the hydrochloric acid gas can either be caused to pass into the generating flask or into water contained in the vessel C. For the rest, D is a wash-flask containing a small quantity of water to wash the chlorine gas, and E, another wash-flask, containing concentrated sulphuric acid to dry the gas.

When the apparatus is charged, the gas under the generating flask is lighted and the hydrochloric acid gas is not pressed into it until the evolution of chlorine begins to slacken. When sufficient chlorine gas has been prepared, the generation of the hydrochloric acid is stopped and the two-way tap shut off so as to prevent any back suction of the contents of the generating flask into the hydrochloric acid apparatus. A supply of chlorine can be obtained at will by again heating the generating flask and passing in hydrochloric acid. By this means practically all the pyrolusite can be used up, and the disagreeable process of constantly washing up the apparatus is dispensed with.

### Phosphorus Trichloride.



Take a hard-glass stoppered retort. Connect it with a fractionating flask, as shown in fig. 14, taking care that the end of the retort passes below the outlet of the distilling flask. The best way to fix it is to pass a piece of rubber tubing over the neck of the retort, as this is more easily arranged than by boring a cork. In the opening of the retort fix a cork which is bored so as to take a tube

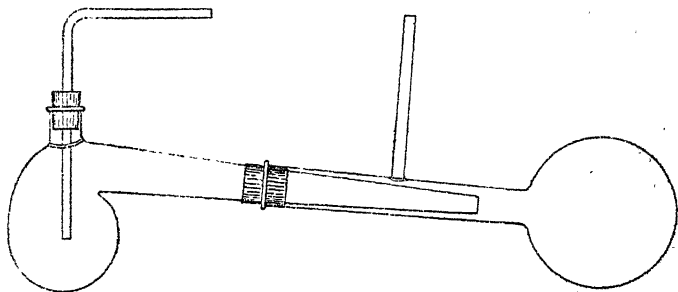


FIG. 14.

bent at right angles. While it is necessary for the tube to fit tightly, the hole should be bored so that the tube can be freely moved up and down; it is advantageous to smear the inside of the hole with a little vaseline. The outlet tube of the distilling flask should be connected with a reversed wash-bottle, which in turn is connected with another wash-bottle containing a strong solution of sodium hydroxide.

When the apparatus is fitted up place in the retort 50 gm. of red phosphorus and clamp the retort on a sand-bath. The distilling flask must be placed in a basin

of cold water, and cold water should be allowed to run continuously into the basin.

Connect a carbon dioxide apparatus with the right-angled tube and fill the apparatus with the dry gas. Now heat the sand-bath so that it is just about red hot; disconnect the carbon dioxide apparatus and connect up with a chlorine generating apparatus. Pass a fairly rapid stream of chlorine into the retort. If the gas is passed in too fast the phosphorus will glow. If this is seen to be the case, move the delivery tube farther away from the phosphorus, and if the glowing still continues, slacken the speed of the chlorine. When the gas is passing at the correct speed the end of the delivery tube will have a lambent flame surrounding it, and this flame may reach to within about 0.5 cm. of the phosphorus, but should not touch it.

Continue to pass chlorine until almost the whole of the red phosphorus has disappeared. There will probably be a little phosphorus pentoxide formed which will partially remain in the tubulus of the retort and partly distil over with the phosphorus trichloride. When the reaction is finished, disconnect the distilling flask from the retort, place one or two small pieces of dry yellow phosphorus into the phosphorus trichloride, fit with a thermometer, connect with a condenser, and distil. The yellow phosphorus is added to convert any phosphorus pentachloride into the trichloride. If by accident almost the whole of the trichloride has been converted into pentachloride, it can be reconverted into the trichloride by the cautious addition of phosphorus—cautious because when there is a large quantity of pentachloride the reaction is very vigorous. In this later case, therefore, the flask should be connected with the condenser before adding the phosphorus.

Phosphorus trichloride is a mobile, unpleasant-smelling

liquid which boils at  $74^{\circ}$ . Care should be taken not to inhale the vapours of the phosphorus trichloride, because they produce the symptoms of a severe cold in the chest.

### Phosphorus Pentachloride



Phosphorus pentachloride is readily prepared by acting upon phosphorus trichloride with chlorine gas. As the pentachloride is a very unpleasant substance to handle and rapidly absorbs moisture from the air, it is best prepared in the bottles in which it is to be preserved.

Take a wide-mouthed stopped bottle, fit it with a rubber stopper in which three holes have been bored. Through the centre hole insert a wide piece of glass tube, through another of the holes fix a right-angled tube which should be connected with a reversed wash-bottle and through this with another wash-bottle containing a strong solution of sodium hydroxide to absorb any escaping chlorine. In the third hole fix a dropping funnel, as shown in the diagram (fig. 15). Fill the dropping funnel with phosphorus trichloride, pass chlorine gas into the bottle, and then open the tap of the funnel and run in 2 or 3 c.c. of the phosphorus trichloride.

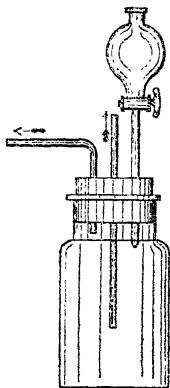


FIG. 15.

Keep a gentle stream of chlorine flowing into the bottle. In a short time all the trichloride will have been converted into pentachloride, which can be judged by the chlorine beginning to pass into the wash-bottle at the same speed at which it enters the bottle; run in another quantity of the trichloride.

The operation of running in small quantities of the trichloride is repeated until a sufficient quantity of the pentachloride has been produced.

If the wide chlorine delivery tube should become stopped up with the solid pentachloride, the chlorine apparatus is disconnected and the tube cleared by pushing a glass rod down it.

### Antimony Trichloride.



Take 50 gm. finely powdered *stibnite* ( $\text{Sb}_2\text{S}_3$ ), place it in a flask and add 230 c.c. concentrated hydrochloric acid. Warm gently on the sand-bath for about an hour and then add a few grms. of powdered potassium chlorate in small quantities at a time, taking care that the mixture does not froth over. Heat for another half-hour and filter through asbestos. Pour the clear yellow solution into about two litres of water and allow the white precipitate of antimony oxychloride ( $\text{SbOCl}$ ) to settle. Decant off the bulk of the solution and then transfer the antimony oxychloride into a Buchner funnel and filter on the pump. Wash the precipitate three times with cold water.

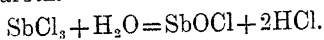
Now transfer the washed precipitate to a flask, dissolve in about 70 c.c. of pure concentrated hydrochloric acid and pass in gaseous hydrochloric acid until no more is dissolved.

Pour the solution into a retort, place in it several pieces of broken porous porcelain, to prevent bumping, and distil from a sand-bath. Every now and then, by means of a glass rod, place a drop of the distillate into water, and as soon as a white precipitate is produced change the receiver. Continue distilling into this receiver until a drop of the distillate solidifies on cooling; this is the antimony tri-

chloride. Again change the receiver and continue the distillation until no more passes over.

The solid crystalline antimony trichloride so obtained should be colourless. If it is brown from contamination with iron, dissolve in concentrated hydrochloric acid and again precipitate as oxychloride, after which proceed as above. The yield of pure product will depend upon the purity of the antimony ore employed. Antimony trichloride melts at  $73^{\circ}$ . Antimony trichloride is soluble in alcohol and carbon disulphide, from the latter of which it can be crystallised.

The first part of the distillate may be poured into water when antimony oxychloride is formed, which may be filtered off, washed and dried. The oxychloride is called powder of Algaroth.



### Antimony Pentachloride.



Grind 30 grm. of metallic antimony into a fine powder and place it in a carefully dried fractionating flask, A,

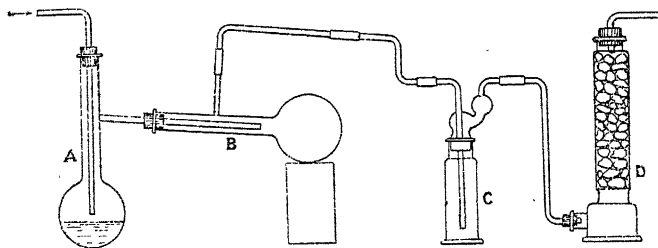


FIG. 16.

fig. 16, which is connected with another fractionating flask, as shown in the diagram.

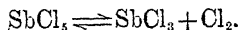


The flask, C, is empty and is simply to serve to catch any antimony pentachloride which may not be condensed in the flask, B. The tower, D, is filled with lime and serves to absorb the excess of chlorine gas.

When the apparatus is connected together, pass dry chlorine gas into the distilling flask, A. Reaction between the antimony and the chlorine will at once ensue, the flask will become very hot, and in a short time liquid antimony pentachloride will be seen to have formed. As soon as the liquid is noticeable the flask should be shaken every few minutes, otherwise the liquid may dissolve a large quantity of chlorine, which may, when it comes in contact with the antimony below the fluid, cause the reaction to become too violent and blow over a portion of the mixture into the flask, B. When nearly all the antimony has been converted into the pentachloride, stop the passage of the chlorine, fit a thermometer into the mouth of the flask, A, in place of the chlorine tube, connect to a vacuum-pump and evacuate the whole apparatus. As soon as the manometer shows that the pressure has been reduced to about 50 m.m. or less, commence to distil and carry on the distillation until all the antimony pentachloride has distilled over. If the pentachloride is not of a light lemon colour, but is reddish in colour, it should be redistilled.

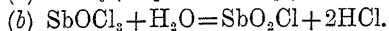
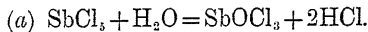
After distilling place in a perfectly dry bottle which is closed with a cork. If glass stoppers are used they soon become set fast through the antimony oxychloride, which is produced from the moisture of the atmosphere, and it then becomes impossible to open the bottles.

The reason for distilling under reduced pressure is that at ordinary pressures antimony pentachloride cannot be distilled without partial decomposition into the trichloride.

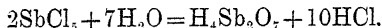


With a vacuum of 22 m.m. the antimony pentachloride distills at a temperature of 79°.

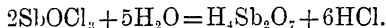
Antimony pentachloride is a strongly fuming liquid with an unpleasant smell. It absorbs moisture from the air with great eagerness, forming a crystalline hydrate,  $\text{SbCl}_5 \cdot 4\text{H}_2\text{O}$ . By the cautious addition of ice-cold water oxychlorides are formed.



By the action of hot water pyroantimonic acid is produced.



The same substance is formed when hot water is added to the oxychlorides.



### Vacuum Distillation.

Substances which are readily decomposable or distil at very high temperatures are often distilled under diminished pressure. The lower the temperature at which a substance is distilled, in general the less the decomposition which takes place.

The boiling-point of a substance is that temperature at which the vapour pressure is equal to the external pressure. It follows therefore that the lower the external pressure the lower the boiling-point of the substance. In other words, by distilling under reduced pressure, the vapour pressure, and consequently the boiling-point of the substance, are lowered.

The apparatus shown in fig. 17 may be used for distillation under reduced pressure. The water-pump, A, is directly connected with the reservoir, B, which may be

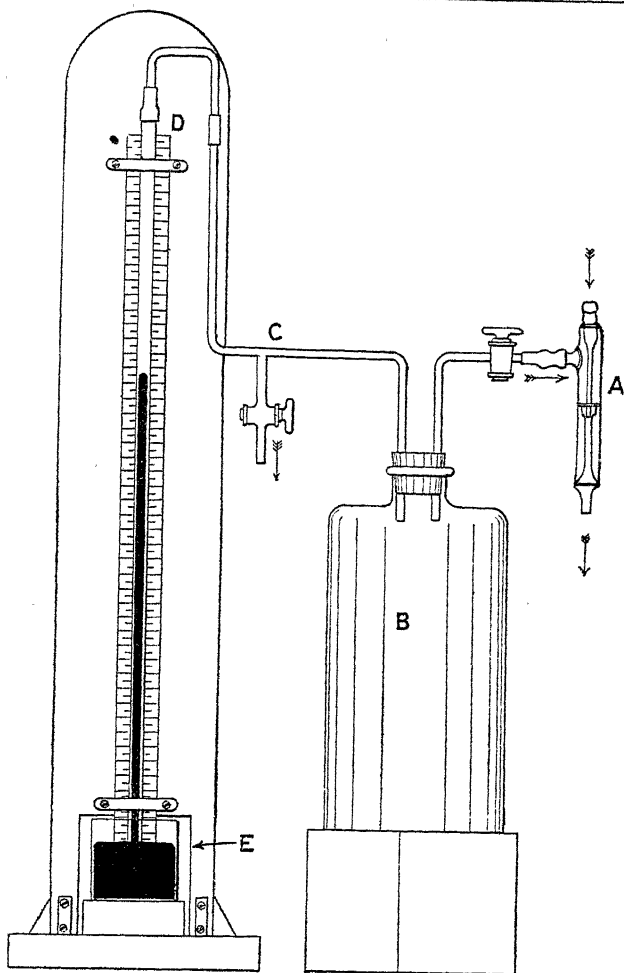


FIG. 17.

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made from a large bottle, for example a Winchester quart. This is connected with a two-way tube, C, one arm of which is in communication with a barometer tube, D, standing over mercury, and the other with the distilling apparatus. The object of having the reservoir is to prevent violent fluctuations of pressure, which would cause the distillation to be uneven. As the pressure decreases, so the mercury rises in the barometer tube, D; the height to which it rises can be directly read off against the millimeter scale fastened against the upright which supports the tube. It is convenient to have the millimeter scale running in a groove so that its position may be regulated in such a manner that the zero mark is always just on the surface of the mercury in the reservoir, E. Before turning off the water from the vacuum-pump always close the tap between the pump and reservoir, to prevent the water being sucked back into the reservoir vessel. If sufficient water pressure to cause a good vacuum is not obtainable, a lead pipe must be connected with the outlet of the pump, as described on page 3; or else a mechanical vacuum-pump, such as a Fleuss, must be employed.

### Tin Tetrachloride.



Tin tetrachloride may be prepared in a similar manner to antimony pentachloride, the apparatus employed being the same as that depicted in fig. 16, p. 78; the distilling flask, A, in this case containing metallic tin, which it is best to have either in the form of a powder or as tin-foil.

As soon as the chlorine is passed, the tin commences to melt in the neighbourhood of the end of the delivery tube,

and in a short time the liquid stannic chloride becomes visible.

As soon as action has ceased, which is usually the case before all the tin has been acted upon, the apparatus is disconnected, the distilling flask connected with a Liebig condenser and the tetrachloride distilled.

B.P.  $113^{\circ}$ . It is important that the tetrachloride should be distilled into a perfectly dry tube, and the condenser tube must also be quite dry. Tin tetrachloride is a thin, colourless, mobile liquid which readily and rapidly absorbs water from the air with formation of a white solid hydrate,  $\text{SnCl}_4 \cdot 3\text{H}_2\text{O}$ . The formation of this hydrate causes the stoppers of bottles containing stannic chloride to become so tightly fixed that it is usually impossible to remove them without breaking the bottle. For this reason rubber stoppers must be used, or better still, the product should be preserved in sealed glass vessels. When added to water great heat is evolved, and a solid hydrate separates out, but if added to a sufficient quantity of water, a clear solution is obtained, which does not deposit hydrated crystals on cooling.

Hot stannic chloride dissolves sulphur, iodine, and yellow phosphorus. The sulphur separates out on cooling as rhombic crystals.

### Sulphur Monochloride.



Place 15 grm. flowers of sulphur in a tubulated retort which is connected with a distilling flask, as illustrated in fig. 14, p. 74. Heat on a sand-bath until the sulphur melts and nearly boils, then pass in a fairly rapid stream of chlorine gas. The chlorine unites with the sulphur,

producing sulphur monochloride, which distils over as it is formed.

When the whole of the sulphur has been used up the apparatus is disconnected, and the sulphur monochloride distilled. As the monochloride boils at  $138^{\circ}$ , it is best not to distil it through a Liebig's condenser, but to connect a wide glass tube about 80 cm. long with the fractionating flask, as shown in fig. 18.

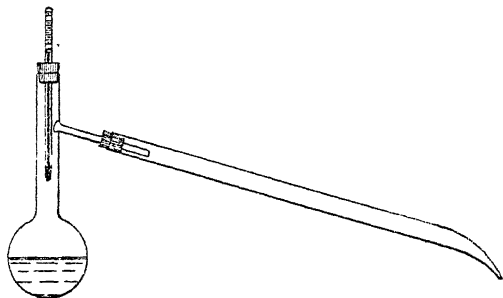
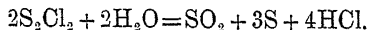


FIG. 18.

The sulphur monochloride is an orange-red, strongly fuming liquid, which acts violently on the mucous membrane, so its vapour should not be inhaled. It readily dissolves sulphur, and for this reason is employed in vulcanising rubber. It is decomposed by water according to the following equation :—



Bromine also unites with sulphur when the two substances are brought into contact. Monobromosulphur, however, is very unstable, and cannot be distilled—except under reduced pressure—without decomposition.

### Aluminium Chloride.



Take a tubulated desiccator jar, as shown in fig. 19, and place it upon a ground-glass plate. Before placing the jar in position, put a clock glass upon the plate, which as nearly as possible fills the inside of the jar. Cut two pieces of thick asbestos board about 4 cm. square, place them in the middle of the clock glass, and upon them

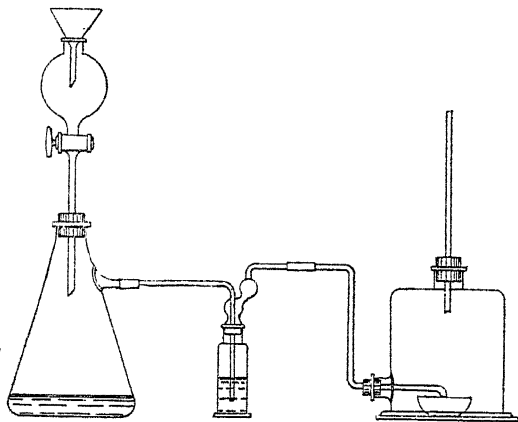
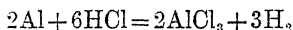


FIG. 19.

place a flat porcelain basin containing 20 grammes of aluminium turnings. As aluminium turnings are always more or less contaminated with grease and oil, they must first be washed with alcohol and then be dried at  $150^{\circ}$ . Now put the jar in position, and pass a rapid stream of hydrochloric acid gas through the side tube. As soon as the jar is quite filled with hydrochloric acid gas, heat from 2 to 4 grammes of aluminium turnings almost to the melting-

point in a crucible before the blowpipe, and drop in through the top of the jar, so that the hot aluminium may fall upon the aluminium in the dish.

Almost at once reaction will commence, and will continue without the aid of further heating until the whole of the aluminium in the basin has been converted into aluminium chloride, provided that a sufficiently rapid stream of



hydrochloric acid gas is caused to pass into the jar. If reaction does not commence when the red-hot aluminium is thrown in, it will be necessary to repeat the operation. Furthermore, should the reaction cease before all the aluminium has been completely acted upon, the hydrochloric acid must be passed for a few minutes to drive out all the hydrogen, and a further quantity of the hot aluminium added.

As the jar gets coated with sublimed aluminium chloride almost immediately, one can only judge that the reaction is continuing through the sides of the jar keeping hot. It usually takes about two to two and a half hours for the whole of the aluminium chloride to be acted upon.

When the reaction has quite finished, lift up the jar, remove the evaporating basin and pieces of asbestos, and scrape the sublimed aluminium chloride from the sides of the jar into the clock glass. Now transfer as rapidly as possible into well-stoppered and carefully dried bottles, or better still, seal up in a glass tube.

Yield about 60 grm.

Another, and perhaps better, method is to prepare it in such a manner that it can be directly sublimed into the bottles in which it is to be kept. In order to do this take a hard glass retort and pass the end through a bored cork which is fitted into the neck of a wide-mouthed bottle.



Through a second hole in the cork a wide glass tube is passed in order to allow the excess of hydrochloric acid gas to pass away. The cleaned and dried aluminium turnings are placed in the retort, through the top of which a glass tube is passed, which is connected with the hydrochloric acid generating apparatus. As soon as the apparatus is full of the gas, the bottom of the retort is strongly heated. In a short time reaction between the aluminium and the hydrochloric acid commences. The aluminium chloride passes into the bottle, where it condenses. From time to time it is necessary to heat the tubulus of the retort to prevent the aluminium chloride from blocking it up, and if reaction ceases, to heat the aluminium in the retort with the bunsen flame. It is important for a rapid stream of hydrochloric acid gas to be passed through the apparatus while the reaction is going on. Should the outlet tube in the collecting bottle become stopped up, it can be cleared by pushing in a strong iron wire.

### Silicon Tetrachloride.



For this preparation it is not necessary to employ pure silicon, but the crude product prepared, as described on p. 124, may be employed, after the bulk of the impurities have been removed by washing with hydrochloric acid.

Take a hard glass combustion tube, such as is used in organic analysis, and fill it loosely with the crude silicon, which has previously been heated for some time to a temperature of  $120^\circ$ , in order to ensure its being absolutely free from moisture. The combustion tube must also be carefully dried: Wrap the tube round with asbestos paper and place it in the iron trough of a combustion

furnace. Connect one end of the tube with a chlorine generating apparatus; the chlorine gas must be dried by passing through concentrated sulphuric acid. One drying flask is sufficient if the gas is taken from a cylinder, but if prepared as required, it is better to employ two drying flasks. Fit a fairly long glass tube, bent at right angles, into the other end of the combustion tube, and connect this with two U tubes of the form illustrated in fig. 20,

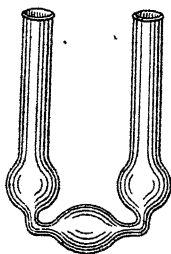


FIG. 20.

the tubes being so connected that the gas must pass first through the one and then into the other. The U tubes should be placed in ice, or better, into a freezing mixture of ice and salt.

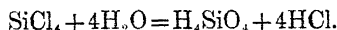
As soon as the apparatus is connected up, pass a slow current of chlorine through it, and light the burners of the furnace. The flames should be so arranged that they do not quite touch the iron trough in which the glass tube rests. The most satisfactory temperature for the formation of carbon tetrachloride is about  $305^{\circ}$ , and it certainly should not exceed  $315^{\circ}$ . By keeping the burners in the position indicated the temperature will be between these points. In a short time liquid silicon tetrachloride will commence to collect in the U tubes; the stream of chlorine gas can then be accelerated. In the course of an hour or two 10 to 15 cm. of the liquid will have collected, and the operation can be continued until the whole of the silicon has been acted upon.

When the reaction has finished, the strongly fuming liquid is transferred to a *thoroughly* dried distilling flask connected to a Liebig's condenser, and the product fractionated. It is most important that all the apparatus—

including the inside of the condenser tube—should be thoroughly dried. The bulk of the liquid will pass over between  $56^{\circ}$  and  $59^{\circ}$ , and is silicon tetrachloride, which must be collected separately. Then the temperature will rise to  $145^{\circ}$ - $146^{\circ}$ , and a fresh fraction consisting of silicon hexachloride,  $\text{Si}_2\text{Cl}_6$ , will distil over.

The two liquids must be kept in bottles closed with rubber or cork stoppers, or better, in sealed glass tubes, because, when kept in glass-stoppered bottles, the stoppers become fixed so that they cannot be removed without breaking the bottles.

Silicon tetrachloride is a colourless, fuming liquid with an unpleasant, catchy smell. When poured into water it decomposes at once, thus:—



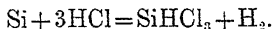
It is owing to the moisture of the air causing this decomposition that the stoppers of bottles containing it become fixed.

The bromide may be prepared in a similar manner to the chloride; it boils at  $153^{\circ}$ , and solidifies at  $-12^{\circ}$ .

### Silicon Chloroform.



I. Silicon chloroform is prepared by passing dry hydrochloric acid gas over dried and heated silicon.



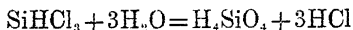
A similar apparatus to that used in the preparation of silicon tetrachloride is employed; hydrochloric acid instead of chlorine being passed over the silicon, which, however, in this case, must be heated between  $450^{\circ}$  and

500°. If the tube is wrapped up in asbestos, then, this temperature is approximately obtained by allowing the iron trough in which it rests to become *just* red hot.

The silicon chloroform collects in the U tubes, and after the reaction is finished, is fractionated from a carefully dried fractionating apparatus. The silicon chloroform distils over between 35° and 40°, the temperature then rises, and silicon tetrachloride passes over.

II. Silicon chloroform can also be produced by passing hydrochloric acid gas over heated copper silicon. Metallic copper remains behind, and a mixture of silicon chloroform, 80 per cent., and silicon tetrachloride, 20 per cent., passes over. As copper silicon is readily obtained on the market, this method is a useful one when large quantities of the chloride or chloroform are required.

Silicon chloroform is a mobile, fuming liquid, and is decomposed by water; it is therefore best preserved

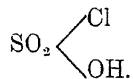


in sealed tubes.

The silicon bromoform may be obtained in a similar manner, but the yield is not so good.

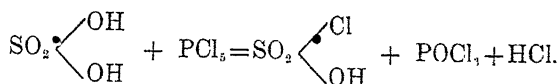
### Sulphuryl Hydroxychloride.

(Chlorosulphonic acid.)



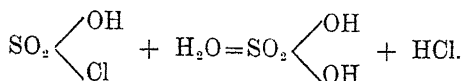
The hydroxyl groups in sulphuric acid can be successively replaced by chlorine. The mono-compound, sulphuryl

hydroxychloride, or chlorosulphonic acid, is prepared by adding the calculated quantity of phosphorus pentachloride to sulphuric acid which is quite free from water.



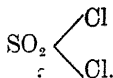
Ordinary concentrated sulphuric acid always contains a small quantity of water, which can, however, be removed by the addition of a small quantity of fuming sulphuric acid.

Take 45 c.c. concentrated sulphuric acid, and add to it 5 c.c. of fuming (Nordhausen) sulphuric acid. Place the mixture in a half-litre flask, and gradually add, in small quantities at a time, 125 grm. of phosphorus pentachloride. When hydrochloric acid is no longer given off, distil the product from a tubulated retort in which a thermometer is fixed. As the chlorosulphonic acid is very corrosive, the thermometer should be fixed in by means of asbestos paper. Pass the end of the retort into a flask which is cooled with water, in the manner usually employed for the preparation of nitric acid. Collect the product which comes over between 145° and 160°. Mix the distillate with about one-tenth its volume of concentrated sulphuric acid, and redistil; this will decompose any chlorides of phosphorus which may have distilled over. Chlorosulphonic acid boils at 156°. It is a strongly fuming liquid which is decomposed upon being dropped into water.



It is employed for purposes of sulphonation in organic chemistry.

### Sulphuryl Chloride.



Take a Woolf bottle with three necks, and through two of the necks pass glass tubes, which reach to the bottom of the bottle—rubber stoppers should be used. Connect one of the tubes with a chlorine generator, and the other with a generator of sulphur dioxide. The middle neck should have a tube bent at right angles to conduct away the excess of gases, and should be connected with a flask containing lime. Now place 20 grm. camphor into the Woolf bottle, stand it in cold water, and pass in sulphur dioxide until no more is absorbed. The camphor and sulphur will gradually form a mobile liquid. When no more sulphur dioxide is absorbed, pass in chlorine until this in turn is no longer absorbed, and then, alternately, sulphur dioxide and chlorine, until the volume of the liquid no longer increases.

When no further increase takes place, or when sufficient sulphuryl chloride has been prepared, pour the product into a fractionating flask, and collect all which passes over below 100°. The fractionating flask and the condenser must be quite dry. On refractionation the sulphuryl chloride will be obtained as a mobile liquid boiling at 68°-70°.

The higher fractions may again be treated with sulphur dioxide and chlorine, when a further quantity of sulphuryl chloride can be obtained.

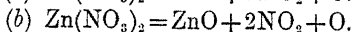
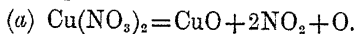
The catalytic action of the camphor in causing the union of the chlorine and sulphur dioxide is very remarkable; one part of camphor being sufficient to cause the union of chlorine, and sulphur dioxide to form fifty parts of sulphuryl chloride.

## CHAPTER V

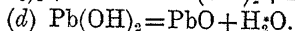
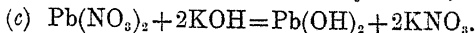
### METALLIC OXIDES

THERE are two general methods employed for obtaining metallic oxides :—

- (1) Dry Method, in which the nitrate or carbonate of a heavy metal<sup>1</sup> is heated to decomposition, as for example :—



- (2) The Wet Method, in which any soluble salt of the metal is taken, and decomposed generally at boiling temperature with an alkali hydroxide, thus :—



Metallic oxides can also be obtained by heating certain metals in the air or by roasting the sulphides in the air.

### Lead Monoxide.



#### *Dry Method.*

Litharge, or lead monoxide, may be prepared by heating lead nitrate strongly upon an aluminium plate. Take

<sup>1</sup> In the case of sodium and potassium the nitrite is produced.

about 10 grm. lead nitrate, and grind to a fine powder, spread thinly upon a thick sheet of aluminium, and heat to low redness with the Bunsen flame. The salt melts, and fumes of nitrogen dioxide are given off, therefore the operation should be conducted in the draught cupboard.

When no more fumes are given off, allow to cool, break the yellowish product off, and grind up in a mortar. The lead nitrate is only partially decomposed by this first heating, so the ground substance must be further heated, either upon aluminium, or upon a large porcelain crucible lid, or in a flat porcelain basin. Continue heating, occasionally turning over with an iron or aluminium spatula, until the whole assumes a uniform yellowish-brown colour. Other oxides, such as copper or nickel, may be prepared by this method, and they are also easier to prepare than lead oxide, which requires a considerable amount of care in order to obtain a pure and homogeneous product.

Aluminium is employed to heat the nitrate upon, because fused lead nitrate acts upon the glaze of porcelain, and if an iron plate is employed, the oxide becomes contaminated with oxide of iron.

#### *Wet Method.*

Prepare 150 c.c. of a boiling 15 per cent. solution of potassium hydroxide and pour *into* it, while still boiling, 100 c.c. of a boiling 20 per cent. solution of lead acetate, stirring all the time. At first a white precipitate of hydrated lead oxide is produced, but this rapidly becomes converted into an orange-coloured heavy precipitate, which falls to the bottom of the beaker. Filter off while still hot, and wash with hot water: finally spread on a porous plate to drain and dry at 100°.

By altering the concentration of the potassium hydroxide considerable variations in colour and appearance of the

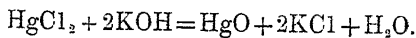


oxide can be caused to occur. Thus with a boiling 75 per cent. solution of potassium hydroxide, the litharge is obtained as beautiful brownish-red crystalline spangles. The lead acetate should be poured in slowly, and must be boiling. •

### Yellow Mercuric Oxide.



Dissolve 30 grm. mercuric chloride in 500 c.c. hot water, and pour the solution with stirring into 300 c.c. of a 10 per cent. solution of potassium hydroxide. Filter and wash well with hot water, spread upon a porous plate to drain, and finally dry in the steam oven.



A bright orange-red variety can be obtained by mixing a boiling 30 per cent. solution of mercuric chloride with a boiling saturated solution of barium hydroxide.

### Red Mercuric Oxide.



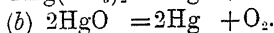
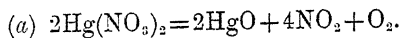
#### 1. *Dry Method.*

Commercially, red mercuric oxide is usually prepared by the dry method.

Heat gently 10 grm. of mercuric nitrate in a porcelain crucible, using a very small flame, until red fumes of nitrogen peroxide cease to be given off. At this stage, if a cold porcelain basin or a test tube containing cold water is held over the crucible, a grey deposit of mercury will condense upon the surface. Now remove from the crucible

and grind up the red oxide. The reaction which takes place when mercuric nitrate is heated is common to all the nitrates of the heavy metals.

But in the case of mercury the heating must be very cautiously carried out, otherwise the oxide of mercury is in turn split up, when the final product is metallic mercury, thus :—



### Peroxides.

The peroxides are generally prepared by causing the lower oxides to absorb oxygen gas from the air at high temperatures. As an example we will here take lead peroxide, and the preparation of barium peroxide will be found on p. 62. Some of the peroxides may also be prepared in the wet way.

### Lead Peroxide.



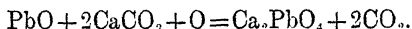
#### *Dry Method.*

Grind up 50 grm. litharge and mix it intimately with 40 grm. finely powdered calcium carbonate. Put the mixture in a fireclay crucible, and heat for about forty-five minutes to a red heat in the muffle or crucible furnace, keeping the furnace open during the operation. While the heating is taking place the mixture should be stirred from time to time with a thick iron wire, or better, with a long clay-pipe stem.

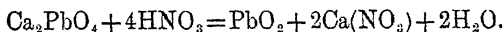
Remove from the furnace, allow to cool, and then grind up in a mortar. Repeat the heating for another three-quarters of an hour, and if, on again grinding, the powder has not a homogeneous, flesh-coloured appearance, again heat.

When the reaction is complete, powder finely; add the powder to about 200 c.c. of warm 2N. nitric acid; allow to stand for an hour or so, with occasional stirring; decant off the nitric acid and repeat the acid washing process. Wash well with hot water, and dry at about 120°. So obtained the lead peroxide is of a dark-brown colour. Commercially, lead peroxide is manufactured in a similar manner.

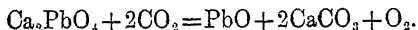
The reaction which takes place is represented by the following equation :—



That is, lead oxide and calcium carbonate, when heated together in presence of air, form calcium plumbate. On the addition of nitric acid the calcium salt is decomposed with precipitation of lead peroxide,



It is of interest to note that when calcium plumbate is heated in a stream of carbon dioxide it is split up and oxygen is evolved, thus :—



On again heating the mixture of lead monoxide and calcium carbonate in presence of air, calcium plumbate is re-formed. The Kassner method for preparing oxygen on a large scale depended upon these facts.

#### *Wet Method.*

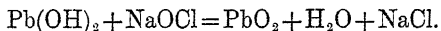
Dissolve 20 grm. lead acetate in 100 c.c. water, and add

it to 100 c.c. of a 4N. solution of sodium hydroxide. Now pass in chlorine gas until, when a drop of the solution is withdrawn and acidified with hydrochloric acid, it no longer shows a test for lead on treatment with sulphuretted hydrogen.

As the chlorine is passed in, the mixture first turns orange-yellow, and then becomes darker and darker, until it is of a uniform dark brown.

Filter off the brown peroxide, wash first with water, then with a little dilute nitric acid, and finally with water, until the washings are no longer acid. Spread on a plate to drain, and finally dry at 120°.

The oxidation to lead peroxide is due to the action of the hypochlorite which is produced when chlorine gas is passed into the cold alkaline solution of lead hydroxide,



Owing to the excess of alkali, part of the lead is present as  $\text{Pb(OH)}_2$ .

Instead of passing chlorine into an alkaline solution of a lead salt, a clear solution of calcium hypochlorite (bleaching powder) may be added to a solution of lead acetate warmed to 60°, until a filtered portion of the solution no longer gives a test for lead.

### Red Lead.

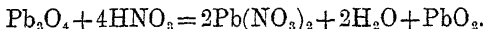


When litharge is spread out in thin layers, and is heated at a moderate temperature—just below red heat—in the air, it becomes gradually converted into red lead. The preparation of red lead is placed here, although it is not strictly speaking a peroxide. The manufacture of red

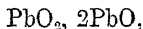
lead is one of great importance, and is very largely carried out by the atmospheric oxidation of litharge at carefully regulated temperatures.

Spread out litharge, which has been carefully ground to a very fine powder, to a depth of about three millimeters on a stout aluminium plate. Rest the aluminium plate on a tripod, and place just beneath it a Bunsen burner fitted with a rose, to distribute the heat. When lighted the flame must be in such a position that it comes within three or four millimeters of the metal plate, but does not actually touch it. From time to time turn over the litharge with an iron spatula. As the heating is continued, the colour of the oxide becomes darker and darker, until finally it becomes of a deep brown. In an hour or two take away the burner and allow to cool. If the oxide is now of a homogeneous scarlet red, then the oxidation is complete: if not, again grind in a mortar, and continue the heating until upon cooling this is the case.

When red lead is treated with nitric acid, a portion of it dissolves, with formation of lead nitrate, and another portion, which consists of lead peroxide, remains undissolved.



The formula of red lead is therefore often written



representing it as being a loose compound of lead monoxide and lead dioxide. Treat about 1 gm. of red lead with nitric acid, then dilute with water, and filter off the lead peroxide on to a weighed Gooch crucible. After washing, dry, and weigh, and see whether the above formula represents the constitution of your red lead.

## CHAPTER VI

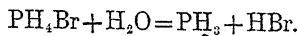
### ACIDS

#### Hydrobromic Acid.

Mix 10 gram. red phosphorus with 20 to 30 gram. fine sand, and place in a distilling flask which has been fitted with a rubber stopper, through which a dropping funnel is passed and connected with three wash-flasks, as illustrated in fig. 21. The middle wash-flask is reversed so as to prevent back suction, and the third flask is half filled with water. The first flask should be about half filled with asbestos wool which has been moistened with water and sprinkled with red phosphorus, so as to prevent any bromine which may be driven over by the vigour of the reaction from passing into the second flask. The first and second wash-flasks should be placed in basins of cold water.

As soon as the apparatus is set up, moisten the red phosphorus in the distilling flask with water, so that a thin paste is formed, and pour 100 gram. (32 c.c.) bromine into the dropping funnel. Allow the bromine to fall on to the red phosphorus drop by drop. As each drop of bromine comes in contact with the red phosphorus a flash of light will be produced. The hydrobromic acid passes through the two first flasks, and is absorbed in water contained in the third flask. The gas should be passed into the water until no further absorption takes place.

If, during the operation, crystals of phosphonium bromide ( $\text{PH}_4\text{Br}$ ) form in the generating flask, they can be caused to disappear by running a little water into the flask.



This, of course, can only be done after all the bromine has been run in from the dropping funnel, but as a rule the crystals only make their appearance after heating has commenced. When all the bromine has been run in, a further quantity of hydrogen bromide can be caused to come off by heating the flask.

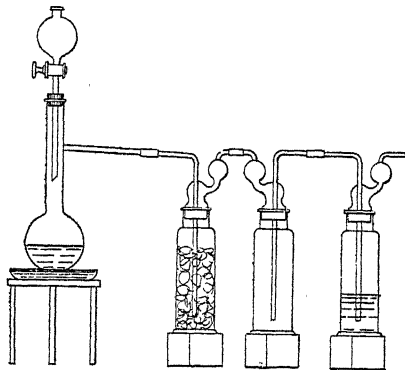


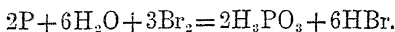
FIG. 21.

A saturated solution of hydrogen bromide has a sp. gr. of 1.78, and contains 82.02 per cent., or  $\text{HBr}$ ,  $\text{H}_2\text{O}$ . On distillation this saturated solution gives up part of its  $\text{HBr}$ , water also passing over with it until the temperature rises to  $125^\circ\text{--}126^\circ$ , when an acid of constant composition distills over, having a sp. gr. of 1.486, and containing 46.83 per cent. of hydrobromic acid,  $\text{HBr}$ ,  $5\text{H}_2\text{O}$ , at a pressure of 760 m.m. Weaker solutions on distillation lose water until the acid finally reaches a concentration

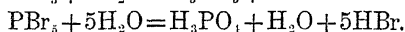
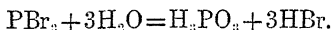
of 46.83 per cent., when it distils at a constant temperature of 125°-126°, at a pressure of 760 m.m.

The solution of hydrobromic acid should be kept in well-stoppered bottles in the dark.

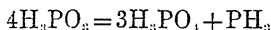
The reaction which takes place when bromine acts upon red phosphorus may be represented by the following equation :—



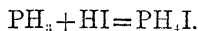
Probably, in the first place, phosphorus tri- or pentabromide is formed and reacts with the water with evolution of hydrobromic acid, thus :—



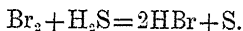
The phosphonium bromide is formed owing to the fact that phosphorous acid, when heated, splits up into phosphine and phosphoric acid, and the phosphine then unites with the hydrobromic



acid, to form phosphonium bromide, exactly the same as when ammonia unites with hydriodic acid to form ammonium iodide.



A solution of hydrobromic acid may also be obtained by passing sulphuretted hydrogen gas, or sulphur dioxide, through a layer of bromine, which is covered with a layer of water. The sulphuretted hydrogen is passed until the solution becomes colourless, and then the deposited sulphur is filtered off through asbestos.





The strength of the solution can be determined by titration with  $\frac{N}{10}$  silver nitrate, using potassium chromate as indicator. Each c.c. of silver nitrate represents 0.0081 gm. of HBr. The acid must be first neutralised. Or it may be titrated with N. alkali.

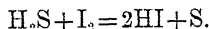
TABLE SHOWING PERCENTAGES OF HYDROBROMIC  
ACID OF DIFFERENT SPECIFIC GRAVITIES.

| Per Cent. HBr. | Sp. Gr. | Per Cent. HBr. | Sp. Gr. |
|----------------|---------|----------------|---------|
| 5              | 1.038   | 30             | 1.252   |
| 10             | 1.077   | 35             | 1.305   |
| 15             | 1.117   | 40             | 1.365   |
| 20             | 1.159   | 45             | 1.445   |
| 25             | 1.204   | 50             | 1.515   |

### Hydriodic Acid.

#### HI.

1. Grind up 30 gm. iodine to a fine powder, and add about 1 gm. of it to 100 c.c. water contained in a flask. Pass a slow stream of sulphuretted hydrogen into the mixture. In a few minutes the iodine will all have dissolved owing to the following reaction taking place:—



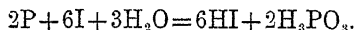
Then add another small quantity of iodine and continue the passage of the sulphuretted hydrogen. Repeat the operation until about one-third of the iodine has been added. Now add the rest of the iodine to the mixture, and allow

to stand with repeated shaking for about half an hour. The iodine will thus dissolve in the already formed hydriodic acid, forming a brown solution. Pass in sulphuretted hydrogen until the brown colour vanishes, *i.e.* until the whole of the iodine is converted into hydriodic acid. When this has taken place, pass a fairly rapid stream of carbon dioxide through the acid in order to drive out the excess of sulphuretted hydrogen. On now shaking the solution, the sulphur will aggregate together, and can be separated by filtering the acid through glass wool.

Hydriodic acid having a specific gravity of 1.7 can be obtained by this method: it distils at 126°-128°.

2. When stronger hydriodic acid is required it must be prepared by passing the gas into cold water, or better, into the cold acid prepared as above.

The gaseous hydrogen iodide can be prepared by acting upon moist red phosphorus with iodine. Take 100 grm. finely powdered iodine, place it in a retort fitted up as illustrated in fig. 22. Also weigh out 6 grm. red phosphorus and make it into a thin paste with 12 c.c. water. To the iodine add 8 c.c. water. The phosphorus paste is placed in the dropping funnel, which, if it has a fairly wide outlet and the red phosphorus has been ground into a thin paste, allows the paste to drop through on opening the tap. From time to time the tap is opened so as to allow small quantities of the paste to run in. This causes the generation of hydriodic acid according to the following equation:—



The rest of the apparatus consists of a U tube containing broken pumice, which is moistened with water and sprinkled with red phosphorus; a safety flask, in case of

back pressure; and the absorption flask, containing water, or a solution of hydriodic acid. All the tubes used in fitting up the apparatus must be fairly wide, because, when they are too narrow, they may become stopped up with crystals of phosphonium iodide. In order to obtain the strongest hydriodic acid, the absorption flask must stand in ice water. After all the red phosphorus has been run in, the flask is heated, when a further quantity of gas is obtained.

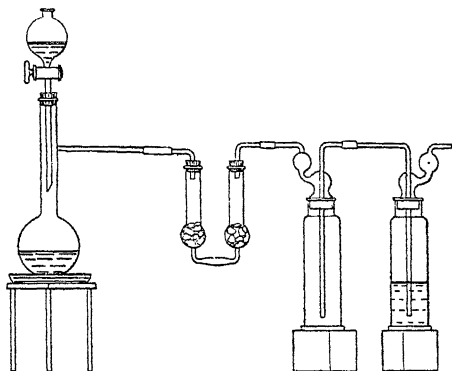


FIG. 22.

The strongest acid has a sp. gr. of 2.0. On distillation this loses some of its hydriodic acid, and eventually an acid of sp. gr. 1.70 distils over at  $126^{\circ}$ . Weaker solutions distil at a lower temperature, but ultimately the temperature rises to  $126^{\circ}$ . In order to prevent oxidation hydriodic acid should be distilled in a stream of hydrogen gas.

TABLE SHOWING PERCENTAGE OF HYDRIODIC ACID  
OF DIFFERENT SPECIFIC GRAVITIES.

| Per Cent. HI. | Sp. Gr. | Per Cent. HI. | Sp. Gr. |
|---------------|---------|---------------|---------|
| 5             | 1.045   | 35            | 1.361   |
| 10            | 1.091   | 40            | 1.438   |
| 15            | 1.138   | 45            | 1.533   |
| 20            | 1.187   | 50            | 1.650   |
| 25            | 1.239   | 52            | 1.700   |
| 30            | 1.296   | ...           | ...     |

### Phosphonium Iodide.

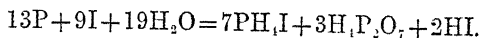


As phosphonium iodide and bromide are obtained in greater or less quantities in the preparation of the hydriodic and hydrobromic acids *loc. cit.*, the preparation is given at this place.

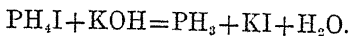
Carefully cut up into small pieces 50 grm. yellow phosphorus and dry with strips of filter-paper. Place the phosphorus in a retort, and add sufficient carbon disulphide to dissolve it; while it is dissolving, pass a slow stream of dry carbon dioxide through the apparatus. When the whole of the phosphorus has dissolved, add, in small quantities at a time, 85 grm. of powdered iodine, keeping the mixture cool by placing the bulb of the retort in cold water. When all of the iodine has been added, slowly distil off the carbon disulphide. As soon as the carbon disulphide has been distilled off, pass the end of the retort through a bored cork, which fits into a wide-

mouthed bottle, and through which a second smaller hole has been bored, through which a narrower tube is passed. Fill the apparatus with carbon dioxide, and then fit a dropping funnel into the top of the retort and, drop by drop, run in 60 c.c. water. When all the water has been run in, replace the funnel by a glass tube, and pass a slow stream of dry carbon dioxide through the apparatus. Heat on the water-bath until no more phosphonium iodide passes over, then carefully stopper the bottle containing the phosphonium iodide.

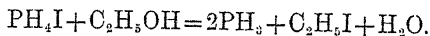
The quantities taken above appear to give the best yield of phosphonium iodide and correspond to the following equation:—



Phosphonium iodide forms large, colourless crystals which possess a diamond-like lustre. They sublime without melting, and fume in the air. When added to water, decomposition takes place, and phosphorus hydrides and hydriodic acid are produced. With potassium hydroxide pure phosphorus trihydride, which is not self-inflammable, is produced.

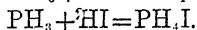
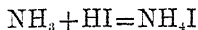


With absolute alcohol it forms phosphorus trihydride and ethyl iodide.



The chief interest of phosphonium compounds is their relationship between ammonium compounds and ammonia. The decomposition of phosphonium iodide to form  $\text{PH}_3$  is an exact analogue to the decomposition of ammonium iodide to produce  $\text{NH}_3$ . Again, just as ammonia unites

to form ammonium compounds with acids, so phosphorus trihydride unites with acids to produce phosphonium compounds.



### Iodic Acid.



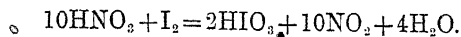
Grind up 15 grm. iodine to a fine powder. Take a 300 c.c. flask containing 150-160 grm. fuming nitric acid. (The sp. gr. of this acid is 1.5, therefore 100 c.c. will represent the quantity required.) Place the flask on a sand-bath; now add the iodine in small quantities at a time, and at the same time bubble oxygen gas through the mixture. All the iodine should be added in about twenty minutes. During the process some iodine may sublime up into the neck of the flask. Should this happen push the sublimed iodine into the flask with a glass rod.

As soon as all the iodine has dissolved, and a white powder of iodic acid has taken its place, remove the flask from the sand-bath, add an equal bulk of water, and transfer to an evaporating dish. Place the evaporating dish on a sand-bath and rapidly evaporate to about one-fourth its bulk. The evaporation must be carried out in a draught cupboard. As soon as sufficient of the liquid has been evaporated off, *i.e.* when about 25 to 30 c.c. remain, cover with a clock glass and set aside to crystallise.

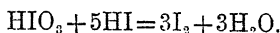
Separate the crystals from the mother-liquor by filtration through asbestos or glass wool. After washing with a very little water, recrystallise from 20 per cent. nitric acid. If the iodic acid so obtained is not colourless it must be again recrystallised.

Yield about 12 to 15 grm.

The reaction is one of oxidation, the iodine being oxidised by the fuming nitric acid.



Iodic acid may be estimated by dissolving it in water, adding a few c.c. of dilute sulphuric acid, then a slight excess of potassium iodide, and titrating the liberated iodine with potassium iodide.

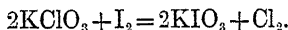


Before titrating the iodine with sodium thiosulphate the solution is first neutralised and then potassium bicarbonate added. Sufficient potassium iodide should then be added to dissolve all the free iodine.

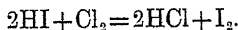
### Potassium Iodate.



It is not necessary to prepare iodic acid in order to obtain the potassium salt, as potassium iodate can be obtained by the direct action of iodine on potassium chlorate in presence of a little nitric acid. Under these conditions the iodine replaces the chlorine in the potassium chlorate. A very small quantity of nitric acid is sufficient to allow the reaction to continue to the end.



This is an interesting instance showing how iodine is able to replace chlorine from its oxygen compounds, the reverse, however, being the case in the hydrogen compounds, thus, *e.g.* :—

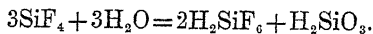


Dissolve 25 grm. potassium chlorate in 120 c.c. boiling water, and to the hot solution add 26 grm. powdered iodine. Add a few drops of concentrated nitric acid. On the addition of the nitric acid chlorine gas will commence to come off. Heat the mixture on the water-bath until chlorine is no longer evolved—from five to six hours. As the reaction proceeds, potassium iodate commences to crystallise out, as it is less soluble in hot water than potassium chlorate. At the end of the reaction allow to cool, filter off the potassium iodate and wash with a little water. Finally recrystallise from boiling water. At 20° 100 parts of water will dissolve 6.92 parts of potassium iodate, and at 100° 32.26 parts.

### Hydrofluosilicic Acid.



Hydrofluosilicic acid is prepared by the action of silicon tetrafluoride upon water,



Place a mixture of equal parts by weight of calcium fluoride and fine sand or powdered glass in a flask placed on a sand-bath, and fitted up as illustrated in fig. 23. Then run in sufficient concentrated sulphuric acid to form a thin paste with the mixture, and gently warm. The gas jar, A, has a small beaker containing mercury at the bottom, below which the delivery tube dips. Above the mercury cold water is placed. As each bubble of gas rises up through the water it is decomposed with formation of silicon tetrafluonate and gelatinous silicic acid. The delivery tube dips below the surface of the mercury, so that the water may not come in direct contact with gas,



because if it does, the silicic acid soon causes the delivery tube to become stopped up. As soon as no more silicon tetrafluoride is produced the aqueous acid and gelatinous silicic acid is separated from the mercury by means of a separating funnel, and then the hydrofluosilicic acid separated from the silicic acid by filtration.

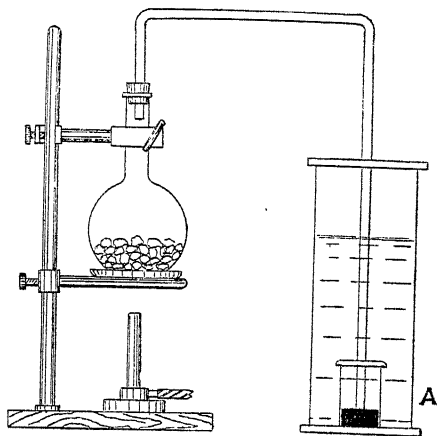
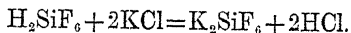


FIG. 23.

Hydrofluosilicic acid is employed as a test for potassium; the potassium salt is practically insoluble in water.



### Phosphoric Acid.



Place 50 grm. yellow phosphorus in a flask with an upright condenser which is ground in at the neck (such flasks are usually called bromine flasks). Then add

600 c.c. of nitric acid (sp. gr. 1.20). The nitric acid employed should be free from sulphuric acid, and *must* not be stronger than 1.20 sp. gr., otherwise an explosion may take place. It is better to make the gravity up to 1.198, but it should not be less than this; if, for example, the gravity is 1.18, the oxidation is extremely slow.

After the nitric acid has been added, place the flask on the water-bath, in a draught cupboard, and heat until all the phosphorus has gone into solution; this takes about twenty hours. If it is desired to complete the oxidation more rapidly, heat on the water-bath for two or three hours, and then remove to a sand-bath and heat to gentle boiling; the condensing tube should not feel hot to the hand more than about half-way up its length.

If a flask with a ground-in condenser is not obtainable, the mixture may be heated in a retort, the end of which passes into a flask, which is cooled by being placed under a tap, water from which is allowed to flow gently over it. As the nitric acid distils over, it is from time to time replaced in the retort, a funnel being used so that the cold acid may not run down the sides of the hot retort and break it.

In either case, as soon as the oxidation is complete, about two-thirds of the bulk of the solution is distilled off, and then the remainder is poured into a porcelain evaporating basin and gently heated on the sand-bath until the temperature rises to 185°; a few drops are now taken out and added to a solution of ferrous sulphate, when the absence of a brown colouration shows that the nitric acid has been completely removed. The phosphoric acid must not be heated above 188°, or else it will be partially converted into pyrophosphoric acid.



As even in getting rid of the nitric acid part of the phosphoric acid may have been converted into pyrophosphoric acid, it should be diluted with about four times its bulk of water, filtered if necessary, and evaporated on the water-bath, until it reaches a syrupy consistency, and finally to a temperature of  $185^{\circ}$ . On standing in a desiccator the phosphoric acid may solidify; if it does not, it should be further evaporated in vacuo, when there will be no difficulty in getting it to solidify on cooling.

Phosphoric acid forms large, colourless, prismatic crystals, which rapidly take up moisture from the air, forming a thick syrupy liquid.

It forms three classes of salts:—

|                          |                          |                         |
|--------------------------|--------------------------|-------------------------|
| $\text{H}_2\text{KPO}_4$ | $\text{HK}_2\text{PO}_4$ | $\text{K}_3\text{PO}_4$ |
| Acid reaction.           | Neutral reaction.        | Alkaline reaction.      |

The reagent in the laboratory called sodium phosphate is hydrogen disodium phosphate.

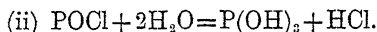
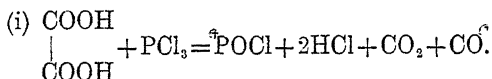
### Phosphorous Acid.



Fit up a flask with a reflux condenser and place it on a sand-bath, now add 64 grm. of powdered crystallised oxalic acid and 54 grm. phosphorus trichloride. Heat gently until the frothing ceases and the liquid becomes clear and free from bubbles.

Pour the fluid while still hot into a porcelain basin and allow to cool in a desiccator. When quite cold it solidifies to an ice-like, crystalline solid, which should be preserved in a well-stoppered bottle. In the reaction the oxalic acid is completely decomposed, and only phosphorus acid remains behind. The first reaction being the formation

of phosphorous oxychloride, which is then converted into phosphorous acid by the water of crystallisation in the oxalic acid.



Phosphorous acid melts at  $70^\circ$ , and on more strongly heating decomposes into phosphoric acid and phosphine.



It readily takes up oxygen, being itself oxidised to phosphoric acid, and is therefore a powerful reducing agent. Although the acid contains three hydrogen atoms, only two of them are replaceable by metals; it is therefore a dibasic acid.

### Hypophosphoric Acid.



Take a large flask of about 2 litres capacity and place in it a solution of 200 grm. copper nitrate in one litre of water, then add 30 grm. of yellow phosphorus and clamp the flask into a large water-bath so that the water in the bath rises just above the solution in the flask.

Now gradually raise the temperature of the water-bath to  $100^\circ$ . As the temperature rises, reaction commences, and a mixture of metallic copper and copper phosphide,  $\text{Cu}_3\text{P}_2$ , begins to be formed. When the temperature of the bath is about  $75^\circ$  the copper phosphide commences to rise to the surface of the solution; here it absorbs oxygen, and a regular decomposition of the copper nitrate sets in,  $\text{NO}_2$

and oxygen being given off, which, with atmospheric oxygen, oxidise the phosphide. Ammonia, phosphorus, and phosphoric acid are also produced.

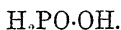
Quantities of about 10 grm. of phosphorus are added from time to time, without taking the flask from the water-bath until the blue colour of the copper nitrate has entirely disappeared. Decant the solution from the precipitated copper and any unacted upon phosphorus, and if necessary filter. Now divide the solution into two equal portions, and neutralise one part with sodium carbonate, and add the other portion to it. On stirring and allowing to stand, the whole mass becomes semi-solid with crystals of hydrogen sodium hypophosphate  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_6$ . Filter off on the pump and wash with a *very* small quantity of *cold*, distilled water. Spread on a porous plate, and when thoroughly drained and dry, preserve in a stoppered bottle.

*Free Acid.*—On adding a solution of lead acetate to a solution of sodium hypophosphate a white precipitate of lead hypophosphate is produced. If this is filtered off, washed with hot water, and then suspended in water and sulphuretted hydrogen passed in, lead sulphide is precipitated and a solution of the free acid obtained. The solution can be concentrated by evaporation, but the evaporation must not be carried too far, or else decomposition will take place. If the fairly concentrated solution is placed in an evacuated desiccator over sulphuric acid, in course of time rectangular tablets belonging to the rhombic system, and having the composition  $\text{H}_4\text{P}_2\text{O}_6$ ,  $2\text{H}_2\text{O}$ , separate out. On leaving these crystals, separated from the mother-liquor, in an evacuated desiccator over sulphuric acid for some weeks, the anhydrous acid is obtained which melts at  $55^\circ$ .

Hypophosphoric acid is contained along with phosphoric

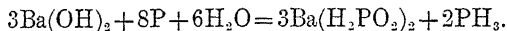
and phosphorous acids in the acid liquor obtained by the slow oxidation of phosphorus in moist air.

### Hypophosphorous Acid.



Boil 10 grm. of yellow phosphorus with about 300 c.c. of a hot saturated solution of barium hydroxide, until the whole of the phosphorus has gone into solution.

As the phosphorus goes into solution hydrogen phosphide is given off, and takes fire spontaneously in the air.



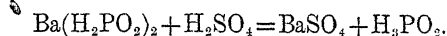
In consequence of this the flask in which the operation is conducted should be fitted with a double-bored cork, through one hole of which a delivery tube is passed; through the other a glass tube which passes just below the solution in the flask, and through which a stream of hydrogen or coal gas is passed so as to drive all the air out of the flask. The delivery tube is dipped below water in a pneumatic trough. Do not commence to heat the mixture until all the air has been driven out of the apparatus.<sup>1</sup>

As soon as all action has ceased, disconnect the apparatus and pass excess of carbon dioxide through the solution, keeping it hot while the gas is passing to prevent the formation of bicarbonate. Filter from the precipitated barium carbonate and evaporate on the water-bath to crystallisation. After standing for twenty-four hours filter off the barium salt, wash with a little cold water, and dry on a porous plate and then in the steam oven. Yield 6 to 7 grm.

In order to obtain the free acid, weigh the crystals of the

<sup>1</sup> The operation should be conducted in the draught cupboard.

barium salt, dissolve in water, and decompose with the calculated quantity of sulphuric acid.

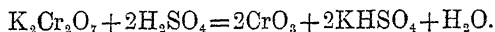


Filter from the precipitated barium sulphate and evaporate on a sand-bath until the temperature rises to  $105^\circ$ . Again filter, while hot, and evaporate further, keeping the temperature at about  $110^\circ$  for about an hour, and finally heat for one-quarter of an hour at  $130^\circ$ . Allow to partially cool, and filter—if necessary—into a stoppered bottle. On cooling in ice the acid solidifies to a white crystalline solid m.p.  $17.4^\circ$ . When it is desired to prepare the acid it is advisable to work with larger quantities than the above.

### Chromic Anhydride.



Dissolve 150 grm. potassium dichromate in 250 c.c. boiling water, and add, while still hot, 190 c.c. concentrated sulphuric acid. The addition of the sulphuric acid must be very cautiously made, otherwise the hot fluid will spirt about. The first portion of the acid must be added very slowly, but after about one-quarter has been poured in the rest can be added more rapidly; the solution of the dichromate should be placed in a porcelain dish before the acid is added. Allow the mixture to stand overnight, and pour off from the potassium hydrogen sulphate which will have crystallised out.

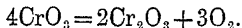


Wash the crystals with a few c.c. water and add to the original solution. Now warm the solution to  $80^\circ$ - $90^\circ$ , add 150 c.c. 4 N. sulphuric acid, and then sufficient water to

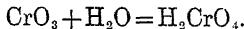
dissolve any chromic anhydride which may have separated. Evaporate on the water-bath until a crystalline scum forms on the surface of the solution. Set aside to cool and allow to stand overnight, when the chromic anhydride will have separated out. A further quantity of crystals can be obtained by a second concentration.

The crystals must be filtered through glass wool or asbestos. When asbestos is used the filtration can be carried out on the pump, and the crystals can then be drained more thoroughly. After filtration spread on a porous plate and leave in a desiccator for twenty-four hours. Transfer the crystals to a funnel stopped with an asbestos plug, and wash on the pump with a little concentrated nitric acid. Again spread on a plate and leave overnight in a desiccator. Finally, to drive off the last traces of nitric acid, heat in a porcelain basin on a sand-bath, continually turning over with a glass rod, until, when a rod moistened with ammonia is held over it, white fumes are no longer produced. On no account may the crystals be heated sufficiently to melt them.

Chromic anhydride forms deep red, needle-shaped crystals, m.p. 192-193, when they form a reddish-brown liquid which solidifies on cooling to a hard, crystalline, brittle, dark-red mass. On further heating to above 250° decomposition takes place,



The crystals dissolve in water to form a yellow solution of chromic acid,



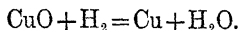
Commercial chromic acid, which is used for charging batteries, is a mixture of chromic anhydride with sulphuric acid and potassium sulphate.



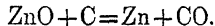
## CHAPTER VII

### PREPARATION OF METALS AND METALLOIDS

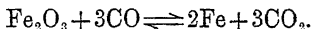
THE methods for obtaining the metals from their compounds are practically all methods of reduction. The reductions may, however, be carried out in a great diversity of ways. Thus, by passing hydrogen over heated copper oxide, metallic copper and water are produced,



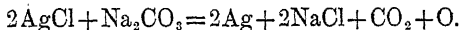
Or the reduction may be carried out by means of carbon,



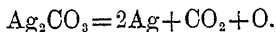
Again, carbon monoxide may be employed,



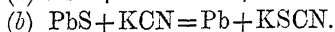
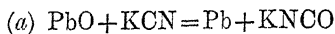
Another method is to fuse a metallic salt with fusion mixture, as, for example, silver chloride,



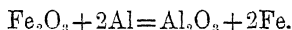
This reaction is, however, only possible where the carbonate first produced is readily decomposed, and where the oxide is also not stable at high temperature, and is, therefore, not of general applicability,



Potassium cyanide is also a very useful reducing agent, as at its fusion temperature it is able to reduce many metallic oxides and sulphides to the metallic state.



A method of very wide applicability, which has recently been introduced, is to act at high temperature upon metallic oxides, sulphides, or sulphates with another metal which has a greater affinity for oxygen or sulphur than the compound with which it is brought into contact. Metallic aluminium is the metal most generally employed, but magnesium and metallic calcium can likewise be used. With ferric oxide the reaction is as follows :—

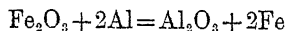


In most cases it is not necessary to heat the whole of the mixture in order that the reaction may take place, but it is only necessary to start it at one point in the mixture, and the reaction being exothermic, so much heat is given out, that it causes reaction to spread throughout the whole mass. The heat produced in the reaction is extremely high, and as it is very much localised, even the most refractory metals may be melted.

The powerful reducing action of aluminium is understood by an examination of the heat of formation of  $\text{Al}_2\text{O}_3$ , which is about 360,000 cal., while that of potassium, to form  $\text{K}_2\text{O}$ , is 97,000.

### Metallic Iron.

Mix together molecular proportions of dry ferric oxide and powdered aluminium. Roughly powdered aluminium or small



turnings is the best form to employ, and not the excessively fine powder, which is used as a pigment. Place the

mixture of ferric oxide and aluminium in a crucible capable of holding about 300 grm., and stand the crucible inside a wider crucible. Then make a fuse mixture of 60 parts of very fine aluminium powder, and 600 parts barium peroxide. In the middle of the mixture in the crucible, dig a hole about 2 cm. deep, and fill it with the fuse mixture, bringing the mixture to a little heap in the centre.

In order to ignite the fuse, fasten a taper on to a stick, and bring the lighted taper into contact with the fuse. The fuse will take fire, and the great heat given out will cause reaction to take place between the ferric oxide and the aluminium, which will continue until the whole of the contents of the crucible have entered into combination. The heat is so intense that the crucible is often broken. When cool, if the crucible has not broken, it is usually necessary to break it in order to obtain the regulus of iron, which is at the bottom of the crucible, covered with fused  $\text{Al}_2\text{O}_3$ . The crucible employed should be lined with magnesia, because the fused aluminium, being basic in character, unites with the silica in ordinary crucibles and destroys them; it also interferes with the smoothness of the reaction.

### Thermit Process of Welding.

The above method for preparing metallic iron of high purity, and of at the same time obtaining very high temperatures, has been employed by Dr. H. Golschmidt in his well-known 'Thermit Welding Process.' There are two methods employed. The one depends only upon the enormous heat developed during the reaction; in the other the molten metal itself causes the welding.

Supposing it is desired to weld two pipes together, then the first method is employed. The two ends of the pipes

are well cleaned with a file or emery paper, and are then clamped together, and a sheet-iron mould is placed round them. The required quantity of thermit is then caused to react in a crucible, and the contents of the crucible immediately poured into the mould. Molten aluminium oxide (corundum) is floating on the surface of the fused mass, and this first comes in contact with the pipes, thus protecting them from the fused iron, which would otherwise burn through them. The molten mass rapidly raises the temperature of the pipes to the welding-point, and then the set screws which hold the clamps are tightened up, thus pressing the ends of the pipes together.

In the second method, which has been much used for welding tram rails, the molten metal is used to unite the ends. In order to do this a conical crucible has a hole in the bottom (fig. 24), which can be closed by an iron disc

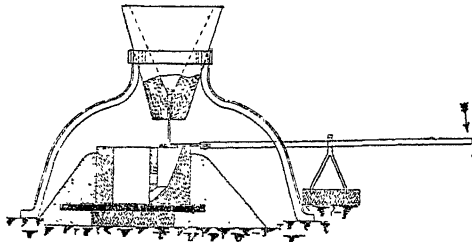


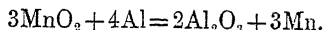
FIG. 24.

covered with a layer of sand (the sand is to prevent the iron disc being burned through). When the reaction is finished the iron disc is pushed to one side, and the molten metal runs out and welds the rails.

### Metallic Manganese.

Manganese can be prepared in a similar manner to iron

by mixing equivalent proportions of dry finely powdered pyrolusite and aluminium,

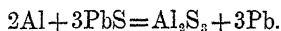


Owing to the high fusing-point of manganese it is not usually obtained as a completely fused mass, but generally more or less broken up. It is, however, quite easy to separate it from the corundum. When larger quantities are worked with, there is no difficulty in fusing the manganese.

**Chromium** can be obtained from chromium sesquioxide. Many other metals are also readily prepared. Certain metallic alloys, such as copper silicon, ferro-chrom, etc., are now manufactured by this process ; so also is silicon.

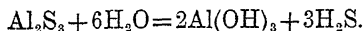
### Aluminium Sulphide and Metallic Lead.

By mixing equivalent proportions of aluminium and of galena, and placing the crucible containing the mixture into a crucible furnace (p. 9), the top of which is kept off, and strongly heating, aluminium sulphide and metallic lead are obtained,



When reaction has finished, the molten liquid is poured into a clean sand-bath. The lead settles at the bottom, and is covered with a layer of fused aluminium sulphide. When cold, there is no difficulty in detaching the metallic lead from the aluminium sulphide.

The aluminium sulphide so produced is of a pale-greenish colour. It decomposes water with evolution of sulphuretted hydrogen, and is acted upon by moist air,

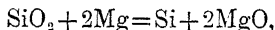


For this reason it is necessary to keep it in well-closed bottles.

## Silicon.

### I. *Amorphous.*

Grind up in a mortar 60 gramm. of thoroughly white sand, and intimately mix with 48 gramm. of well-dried powdered magnesium. Spread this mixture upon an iron sand-bath to a uniform depth of about 1 cm. Heat the bottom of the sand-bath so that it is almost red hot, and then lower the blowpipe flame until only a fine-pointed flame is left, and heat one edge of the sand-bath to bright redness. The high temperature will cause reaction to take place between the silica and the magnesium,



and the mixture will glow brightly at the point where it has been heated.

The reaction gradually spreads through the whole of the mixture. When the reaction is finished, allow the mixture to cool, then scrape off from the sand-bath, and treat in a beaker or evaporating basin, with an excess of hydrochloric acid (1:2). The hydrochloric acid dissolves out the magnesium oxide, and leaves behind the silicon and any unchanged sand, and there is always a certain quantity owing to the magnesium at the surface of the mixture combining mainly with the oxygen of the air, possibly also to a portion of the amorphous silicon burning after it has been produced.

When the mixture is treated with hydrochloric acid, usually a certain quantity of silicon hydride ( $\text{SiH}_4$ ) is produced, which takes fire spontaneously in the air. The formation of the hydride is probably due to a portion of the silicon combining with the magnesium to form

magnesium silicide, and this then forms the hydride on treatment with hydrochloric acid.

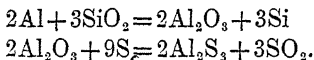
After washing with water and drying, a brown amorphous powder is obtained. This is always contaminated with small quantities of sand, but for the preparation of silicon tetrachloride (p. 87) and of silicon chloroform this does not matter.

## II. *Crystalline.*

Make a thorough mixture of 56 grm. powdered aluminium, 180 grm. powdered sand, and 288 grm. flowers of sulphur. Put the mixture into a crucible and place in a crucible furnace. Bring the temperature of the furnace to a full red heat, then open the furnace, and if reaction has not commenced, drop a little powdered magnesium on to the top of the crucible. Reaction will commence between the aluminium sand and sulphur, and will continue until the whole of the mixture has entered into reaction. As soon as the reaction is complete, the furnace may be turned out, and the crucible and its contents allowed to partially cool. Before the crucible is quite cool, remove it from the furnace, place it in an evaporating basin containing water, and pour water on to it. A vigorous reaction will ensue, and probably the crucible will break. After the reaction has moderated, remove the pieces of crucible from the mixture, and add a slight excess of hydrochloric acid. The silicon may now be found in the form of one or two large crystalline masses, in which case there is no difficulty in separating it from any gangue. Or it may be in the form of a number of varying-sized pellets of crystalline form. In this case the larger pieces may be picked out, and then the remainder treated with hydrochloric acid.

Silicon obtained by this method is a crystalline substance which has rather the appearance of graphite.

The reaction may be represented by the two following equations:—



Theoretically, the whole of the aluminium should be obtained as sulphide, but almost invariably a good deal of oxide remains behind, and as this has been treated to a very high temperature, it is a very difficult matter to get it into solution by treatment with acids.

### Boron.

Amorphous boron may be prepared in a similar manner to amorphous silicon, but the product so obtained is very impure. It can, however, be used to prepare certain boron compounds, such as the chloride or bromide. The preparation of the pure product is a very long and tedious process. [Consult Moissan, *Zeit. f. anorg. Chem.*, 13, 366, or *Central Blatt*, 1895, II. 858.]

### Pure Silver from Silver Residues or Alloys containing Silver.

#### *Dry Method.*

The silver residues are treated with a slight excess of hydrochloric acid, in order to convert them all into silver chloride. Alloys are first dissolved in nitric acid, and then hydrochloric acid is added to the solution so obtained. The silver chloride, whether obtained from residues or alloys, is filtered off and well washed with hot water. After washing, the chloride is dried in the steam oven, and then mixed with two parts by weight of anhydrous

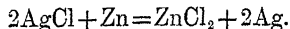


sodium carbonate and 0.25 parts of sodium peroxide or potassium nitrate.

A graphite crucible is now heated to bright redness in a muffle furnace, and the mixture placed into it in small quantities at a time; the addition being regulated so as to prevent frothing over. As soon as all the mixture has been added, the furnace is closed, and the heating continued until the silver has melted together. When all the silver is completely fused, the crucible is removed from the furnace and the melted silver poured into a large quantity of cold water. The granulated silver is then picked out, washed with a little water, and dried.

*Wet Method.*

The carefully washed silver chloride is placed in a beaker with warm dilute sulphuric acid, and then a few small pieces of zinc brought into contact with the silver chloride. The zinc gradually goes into solution, and the silver chloride becomes decomposed,



As soon as all the silver chloride is decomposed the remainder of the zinc is dissolved, the finely powdered silver is filtered off, washed with dilute sulphuric acid, and finally with distilled water. After drying, the silver may be melted down in a crucible, or if required for making silver nitrate, directly dissolved in nitric acid. Cf. p. 12.

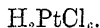
**Silver Nitrate.**

In order to prepare silver nitrate the silver is treated in a beaker covered with a clock glass, with nitric acid 1 : 1, until it has completely dissolved. The sides of the beaker and the cover glass are then washed down with distilled

water, and the contents of the beaker transferred to an evaporating basin. The evaporating basin is placed on a water-bath and the solution evaporated down to dryness in order to drive off the excess of nitric acid.

The silver nitrate is dissolved in water, evaporated to crystallisation and set aside, covered with a clock glass, and allowed to crystallise. After about twenty-four hours the crystals are collected on a filter and washed with a very little cold water, roughly dried by spreading on filter-paper, and finally dried in a desiccator over solid potassium hydroxide.

### Hydrochloroplatinic Acid.



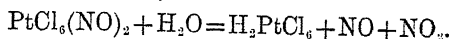
(From scrap platinum and platinum residues.)

#### *I. From Platinum Scrap.*

The scrap platinum is cleaned by boiling for some minutes in concentrated hydrochloric acid, and then washing with water. It is then placed in a roomy flask and covered with concentrated hydrochloric acid. The acid is brought to the boil, and then nitric acid added in small quantities at a time, until the whole of the platinum has been brought into solution, and only a black powdery residue remains; this is probably iridium, which is almost invariably contained in commercial platinum.

The solution is poured off from the residue into a porcelain evaporating basin and evaporated on the water-bath to a syrupy consistency. It is then dissolved in a little water, placed in a large beaker, and equal quantities of sodium carbonate and formate are added until the solution is distinctly alkaline: care must be taken not to allow the solution to effervesce over. The mixture is now

heated to boiling, and in a few minutes the whole of the platinum and any dissolved iridium will be precipitated out. The supernatant liquid is poured off and washed several times by decantation, first with hydrochloric acid and then with water. Filter off (this is best done in a weighed Gooch crucible), and ignite strongly before the blowpipe; again weigh the crucible, and thus ascertain the weight of the platinum. This ignition renders any iridium insoluble in *aqua regia*. Now treat with hydrochloric acid and nitric acid as above, and warm gently until no more of the metal goes into solution. Evaporate to small bulk on the water-bath, add a considerable quantity of water, and again evaporate down. The evaporation with water decomposes *nitroplatinic chloride*, which is always formed in greater or less quantities,

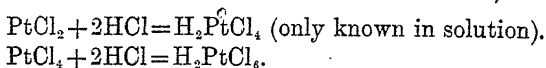


As soon as the solution has evaporated to small bulk take up with hydrochloric acid and again evaporate down; this is to drive off the remainder of the nitric acid. Should nitric acid still be present the evaporation with hydrochloric acid must be repeated.

On adding water a dark brown solution will be obtained owing to the presence of *hydroplatinous acid*. In order to convert this into hydroplatinic acid saturate the warm solution with chlorine, when it will become much lighter in colour; filter from any iridium, evaporate to a syrupy consistency, and cool in a desiccator. On standing the whole substance becomes a brownish-yellow mass of crystals.

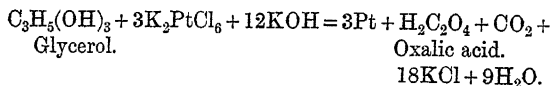
If the original weight of the platinum taken is known, there is no difficulty in making up a solution of any desired strength.

Platinum forms two oxides, platinous oxide,  $\text{PtO}$ , and platinum oxide,  $\text{PtO}_2$ . From these are derived platinous chloride and platinum chloride, which, with hydrochloric acid, form hydroplatinous acid and hydroplatinic acid,



## II. *From Platinum Residues.*

Platinum residues usually consist mainly of potassium and ammonium chloroplatinate. Evaporate the whole of the residues to dryness, digest with two or three quantities of hot water, and filter. Pour the aqueous solution into a strong solution of caustic soda containing 8 per cent. of glycerol, and boil. The platinum is deposited as a black powder.

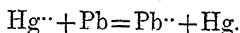


Wash the platinum with water, then with hydrochloric acid, and finally with water. Filter on a weighed Gooch crucible, dry and ignite and weigh. Now treat as described under I.

## Purification of Mercury.

Mercury may be purified by leaving it in contact with 20 per cent. nitric acid for some time. The impurity of mercury is due to the presence of metals which are more electropositive than mercury, *e.g.* zinc and lead. These metals are amalgamated with the mercury, and are therefore there in the metallic condition. Now if a piece of

lead or zinc is placed in a solution of a mercury salt the metal goes into solution and metallic mercury is produced; in other words, the metal passes into the ionic condition, and the mercury assumes the atomic state, thus:—



It is not necessary to actually add a salt of mercury, because the nitric acid dissolves sufficient of the mercury for the above reaction to take place.

In order that the whole of the mercury may come in contact with the nitric acid, Ostwald employs a glass tube, the lower end of which is drawn out and bent over in the form of a siphon (fig. 25). The tube is filled up to the top of the siphon with mercury, and then nearly to the top with 20 per cent. nitric acid. A small funnel, A, the end of which is drawn out into a capillary, is placed in the mouth of the tube. Mercury is then poured into the funnel, which, as the opening is very small, runs out in the form of very small drops. A very large surface of the mercury thus comes in contact with the nitric acid. As the volume of the mercury rises above the bend of the siphon, so the metal siphons over and furthermore is obtained quite dry, because the aqueous solution is behind the mercury. After passing two or three times through this apparatus the mercury is practically pure.

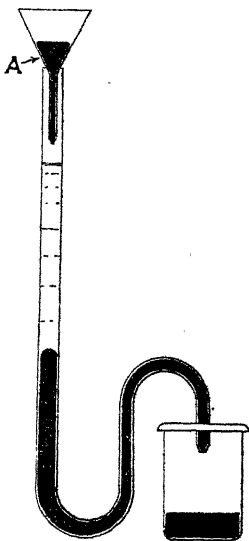


FIG. 25.

An even more satisfactory method is to place a layer of mercury on the bottom of a glass jar, and to cover it with

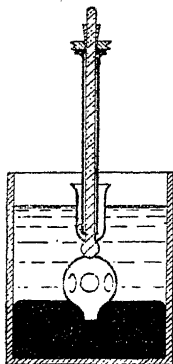


FIG. 26.

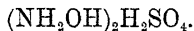
a deep layer of 20 per cent. nitric acid. A glass stirrer of the form shown in fig. 26 is then fixed so that the end of it dips just below the mercury, and is then caused to rotate rapidly by means of a water turbine or electro-motor. The mercury passes up the centre of the stirrer and is thrown out from the side holes in very fine globules. This form of apparatus has the advantage that no attention is required after it has been set up. The mercury is then well washed with water and dried with pieces of filter-paper. It

may finally be filtered through a filter-paper which has two or three fine holes pierced in it by means of a pin.

## CHAPTER VIII

### SPECIAL PREPARATIONS

#### Hydroxylamine Sulphate.



PREPARE a saturated solution of commercial sodium nitrate containing 146 grm. (2 mol.) of the solid salt (this is calculated on the assumption that commercial sodium nitrite contains 95 per cent. of  $\text{NaNO}_2$ ), and a nearly concentrated solution of sodium carbonate containing 106 grm. of the anhydrous salt (1 mol.). Mix these two solutions together, cool to  $2^\circ\text{--}3^\circ$  by standing in a mixture of ice and salt, keeping the solution well agitated by means of a mechanical stirrer. As soon as the mixture is sufficiently cool, pass in sulphur dioxide until it becomes slightly acid, taking care that, at any rate, the temperature does not rise above  $5^\circ\text{C}$ .

To the solution so obtained add 0.5 c.c. concentrated sulphuric acid, and heat on the water-bath to a temperature of from  $90^\circ\text{--}95^\circ$  (not higher) for forty-eight hours.

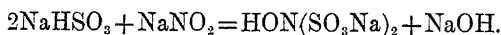
At the end of this time neutralise the solution with sodium carbonate, using methyl orange as an indicator. Evaporate the neutral solution on the water-bath until the bulk is not more than 1200 c.c. Transfer to a beaker, and stand in ice-cold water for an hour or two, and filter from

the deposited sodium sulphate. Wash the sodium sulphate with a *very* little ice-cold water, and add the washings to the mother-liquor.

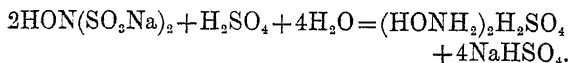
On evaporating the solution down to about one-third of its bulk, and allowing to cool, hydroxylamine sulphate will crystallise out. Filter off the hydroxylamine sulphate. Now add a small quantity of water to the mother-liquor and stand in ice, when a further small quantity of sodium sulphate will crystallise out. On again evaporating, a further yield of hydroxylamine sulphate will be obtained. Mix the two crops of crystals together and purify by recrystallisation.

Yield about 100 gm.

By the action of the acid sodium sulphite, produced when the solution of sodium carbonate is saturated with sulphur dioxide, upon the sodium nitrite sodium oximidosulphonate is produced, thus:—



On warming the oximidosulphonate with a small quantity of sulphuric acid, it is converted into hydroxylamine sulphate,



On then adding sodium carbonate any free acid is neutralised, and the acid sodium sulphate is converted into the normal salt.

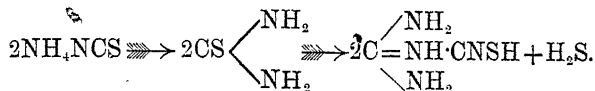
### Hydrazine (Diamid).



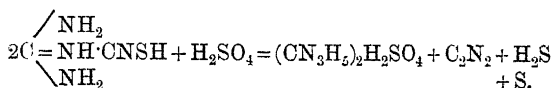
When dry ammonium thiocyanate is heated to a tem-



perature of about  $200^{\circ}$ , it is converted into thiourea, which then splits off hydrogen sulphide, and guanidine thiocyanate is formed, thus:—



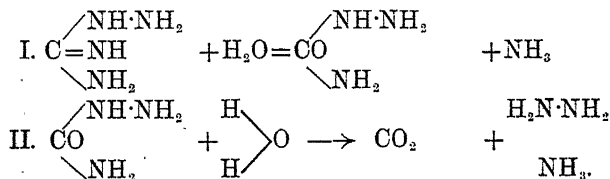
On treatment with concentrated sulphuric acid, the guanidine thiocyanate is decomposed with formation of guanidine sulphate,



When acted upon with concentrated nitric acid, nitroguanidine,  $\text{C} \begin{array}{l} \diagup \text{NH} \cdot \text{NO}_2 \\ \diagdown \text{NH}_2 \end{array}$ , is produced, which on reduction

with zinc and acetic acid yields amido-guanidine,  $\text{C} \begin{array}{l} \diagup \text{NH} \cdot \text{NH}_2 \\ \diagdown \text{NH}_2 \end{array}$ . On hydrolysis, amido-guanidine splits up

into carbon dioxide, ammonia, and hydrazine. The reaction appears to take place in two stages. In the first place, ammonia and semicarbazid are formed, and then the semicarbazid splits up into carbon dioxide, hydrazine, and ammonia, thus:—



*Preparation.*—I. **Guanidine.**—Take 500 grm. ammonium

thiocyanate, place it into a round-bottomed flask of about one and a half litres capacity, and put the flask in an oil-bath. Keep the oil-bath at a temperature of  $190^{\circ}$  to  $195^{\circ}$  for twenty hours. The temperature must not be allowed to fall below  $190^{\circ}$ , otherwise it will be necessary to heat for a longer period; neither should it rise above  $195^{\circ}$ . The heating may be done in two or three operations. The ammonium thiocyanate melts, and hydrogen sulphide is given off. At the end of the time, pour the hot and fluid substance into an evaporating basin and allow to cool. On cooling, the guanidine thiocyanate separates readily from the basin in the form of a cake, which, on breaking, shows a crystalline fracture. If a sample of it is required, it may be dissolved in hot water, from which it crystallises in large leaflets, m.p.  $118^{\circ}$ . The yield of guanidine thiocyanate is 50 per cent. of the ammonium thiocyanate taken.

**II. Nitro-guanidine.**—Break the crude guanidine thiocyanate up into a rough powder, and add it to 220 grm. concentrated sulphuric acid contained in a large evaporating basin. A vigorous reaction ensues, and large quantities of gas are given off. As these are poisonous, and also turn everything red with which they come in contact, it is best to apply a light, and cause them to burn as they are given off. A beautiful purple flame is produced owing to the combustion of the cyanogen. When the reaction is finished, pour the thick solution into a flask, washing the sides of the basin with a little strong sulphuric acid. To the turbid liquid, which contains free sulphur floating in it, add 110 c.c. fuming (Nordhausen) sulphuric acid, containing 20 per cent. of anhydride (the ordinary fuming acid usually contains about this quantity). Cool the contents of the flask first under the tap, and then with ice to  $0^{\circ}$ . Also cool 170 c.c. of fuming nitric acid to  $0^{\circ}$ . When

both are cooled, add the nitric acid to the guanidine solution, shake up, and as soon as the liquid begins to foam vigorously, pour it into two litres of ice-cold water, containing plenty of broken ice. Allow to stand for about half an hour, and then filter off, on a large Buchner funnel, the bulky nitro-guanidine which has separated out in the form of yellow silky needles. When the nitro-guanidine has drained, remove it from the pump, and mix it up with 250 c.c. of ice-cold water, and again filter. Now spread on a porous plate. So obtained, the nitro-guanidine is of a light yellow colour; it contains a small quantity of sulphur as an impurity. Recrystallise a sample from boiling water. The yield of nitro-guanidine is about 50 per cent. of the guanidine thiocyanate.

The pure nitro-guanidine forms almost colourless hairy crystals, melting at  $230^{\circ}$  with evolution of ammonia.

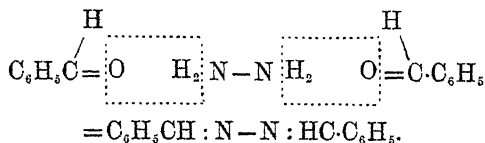
III. **Amido-guanidine.**—Take 120 grm. of the crude nitro-guanidine, and grind it up in a mortar with 350 grm. zinc dust, and add water and powdered ice until a moderately thick porridge is obtained. Then gradually stir in 62 grm. of glacial acetic acid, adding ice at the same time in order to keep the temperature at  $0^{\circ}$ . The addition of the acetic acid should take from three to four minutes. When all the acid has been added, pour into an evaporating basin, and allow the temperature to rise, through reaction taking place, to  $40^{\circ}$ - $45^{\circ}$ . From time to time take out a small test portion and filter it, then add to it a solution of a ferrous salt and caustic alkali. When a purple red colour is no longer produced the reaction is finished. If the red colour still persists at the end of an hour and a half, the mixture may be gently warmed, but should not be heated above  $50^{\circ}$ , when the reaction will rapidly complete itself.

Now filter off on a large Buchner funnel from unchanged zinc and zinc hydroxide, wash twice with hot water. To

obtain the amido-guanidine, add sufficient hydrochloric acid to replace the acetic acid, and evaporate to dryness, the latter part of the operation being conducted on the water-bath. Extract the residue with alcohol; this may best be done by means of a Soxhlet extractor (p. 53). The amido-guanidine hydrochloride can be obtained by evaporating off the alcohol. It is obtained by crystallisation from dilute alcohol in thick crystalline prisms, m.p.  $163^{\circ}$ .

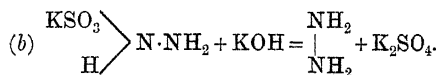
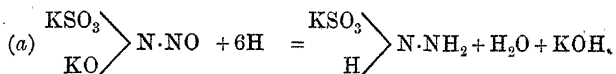
**IV. Hydrazine.**—It is not necessary to purify or even to isolate the amido-guanidine in order to obtain hydrazine. The filtrate from the reduction may be directly employed. Evaporate the solution to about 600 c.c., and then add to it 120 grm. sodium hydroxide dissolved in 220 c.c. water. Place the mixture in a round-bottomed flask, fit the flask with a reflux condenser, and heat to boiling on the sand-bath for eight to ten hours. As the solution is apt to bump vigorously, a considerable quantity of broken porous porcelain should be put into the flask, and it should be heated on a deep sand-bath, so that the sand can come well up round the flask.

On cooling, sodium carbonate separates out; filter from this, and then pour in 140 c.c. concentrated sulphuric acid, when, partially in the heat, but to a larger extent on cooling, hydrazine sulphate separates out. It can be purified by crystallisation from water. It melts at  $256^{\circ}$ . A further quantity can be obtained from the mother-liquors by shaking up with benzaldehyde, when a yellow precipitate of benzalazine is obtained, which is separated from the inorganic salts by extraction with ether.



Hydrazine sulphate can be obtained from the benzalazine by evaporating the ethereal solution to dryness and treating it with excess of dilute sulphuric acid. The mixture is then steam distilled to get rid of benzaldelyde, filtered from a small quantity of resinous matter, and evaporated to dryness. The brown crystalline mass is washed with alcohol and the hydrazine sulphate which remains behind, and can be purified by recrystallisation from water.

Another method for preparing hydrazine, and one which is purely inorganic, is by the reduction of potassium dinitrosulphonate with sodium amalgam. The reaction would appear to take place in two stages.



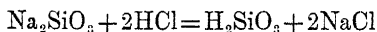
Suspend freshly prepared potassium dinitrosulphonate,  $\text{K}_2\text{SO}_3 \cdot \text{N}_2\text{O}_2$ , in ice-cold water, and gradually add, in small quantities at a time, 2 per cent. sodium amalgam, until the liquid readily reduces Fehling's solution (p. 151). When the reaction is complete, the solution is rendered acid with dilute sulphuric acid, and shaken up with benzaldelyde and warmed, when benzalazine separates, from which hydrazine sulphate can be obtained, as described above. The yield by this method is very poor.

### Colloidal Solutions.

When an alkali silicate is mixed with an acid, if the solution of the silicate is strong, a gelatinous precipitate

of silicic acid is obtained. But if the solution of the silicate is dilute, no precipitation ensues. This is not due to the fact that silicic acid is partially soluble in water, but to the fact that silicic acid is capable of forming a *pseudo* solution, and when a substance forms such a solution it is said to be in the *colloidal* state.

Now a substance which is capable of forming a colloidal solution is incapable of passing through a parchment membrane, but a true solution, such as a solution of sodium chloride, is able to do so. If we take this *pseudo* solution of silicic acid, which also contains a solution of sodium chloride, and place it in a dialyser, the silicic acid can be

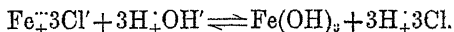


separated from the sodium chloride. A dialyser may readily be made by taking a bell jar which is open at both ends, the bottom being closed by means of a piece of parchment paper, which is tied tightly with string, so that no liquid can run out. The colloidal solution is poured into the dialyser, which is then suspended in water. The sodium chloride diffuses through into the water, but the silicic acid remains in the dialyser, and by continually changing the water in the outer vessel, practically the whole of the sodium chloride will pass through, because the sodium chloride will diffuse through until the concentration is the same in the outer vessel and in the dialyser. When a substance can be obtained in two forms, the soluble or pseudo-soluble, and insoluble, then the soluble or colloidal condition is called **hydrosol**, and the insoluble the **hydrogel**. Many substances show this peculiarity, *e.g.* ferric hydroxide, chromic hydroxide, arsenious sulphide, metallic silver and gold, and many other elements and compounds.

The chief difference between colloidal and true solutions is that colloidal solutions exhibit very slight depression of the freezing-point or elevation of the boiling-point; they have also practically no electrical conductivity. The addition of strong solutions of electrolytes precipitate the substances in the hydrogeal form. When viewed, by the aid of a powerful beam of light, through the microscope, suspended particles can be seen, and therefore colloidal solutions may be regarded as intermediate between solutions and suspensions. When precipitated by means of an electrolyte the precipitate invariably contains a part of the electrolyte. If an attempt is made to completely remove the electrolyte by washing, then the precipitate goes into solution once more.

### Colloidal Solution of Ferric Hydroxide.

Dissolve 100 grm. ferric chloride in 300 c.c. distilled water, and filter if the solution is not clear. This solution will be found to be strongly acid to litmus owing to the hydrolysing action of the water, which may be represented by the equation (see p. 145),



The ferric hydroxide is not precipitated, but imparts a deep brown colour to the solution. If now the hydrochloric acid is cautiously neutralised with ammonium carbonate, equilibrium will be disturbed, and more ferric hydroxide will assume the colloidal condition until the whole of the iron is in this state. The operation is rather tedious, and requires great care; it may be carried out as follows:—

Dissolve 75 grm. powdered ammonium carbonate in

150 c.c. distilled water, and add this solution slowly with constant stirring to the ferric chloride solution prepared as above. The most satisfactory way to add the ammonium carbonate is by means of a siphon from a bottle placed above the solution, the ferric chloride solution being at the same time constantly stirred.

At first the ammonium carbonate may be added fairly rapidly until the iron solution is no longer acid to litmus paper. The ferric chloride solution will now have a dark brownish-red colour, and must at this stage be divided into three parts. Each solution is now treated separately with ammonium carbonate, which must be added drop by drop with extreme caution, taking care that the precipitated hydroxide dissolves before the addition of a fresh quantity of the ammonium carbonate. By having the solution in three portions it is possible, in the case of the mark being overpast, to add one of the other solutions to it, and thus prevent spoiling the whole bulk of solution.

Finally, when all the ammonium carbonate has been added, pour the product into the dialyser or several dialysers: the height of liquid in each dialyser should not exceed 8 to 10 cm. Continue the dialysis for two weeks with a slow stream of tap water continually running through the outside vessel. At the end of this time the solution will still contain small quantities of chloride, and this can only be completely removed by long-continued dialysis with distilled water.

In a similar manner colloidal solutions of chromium and aluminium hydroxide can be obtained. With chromium the starting-point is usually chromic chloride with aluminium the sulphate. With these substances it is better to work with rather weaker solutions.

Colloidal **arsenious sulphide** can be prepared by passing sulphuretted hydrogen into a solution of arsenious acid in



pure water. The solution becomes yellow and the smell of sulphuretted hydrogen vanishes, but no precipitate is produced. The addition of hydrochloric acid or of other electrolyte causes slow precipitation. In fact, on keeping the solution for some time, deposition of the yellow trisulphide gradually takes place.

### MELTING-POINT AND SPECIFIC GRAVITY OF SOME METALS.

|                      | m. p.   | sp. gr.     |
|----------------------|---------|-------------|
| Aluminium, . . . .   | 660°    | 2.58        |
| Antimony, . . . .    | 435°    | 6.62        |
| Bismuth, . . . .     | 269°    | 9.78        |
| Cadmium, . . . .     | 321°    | 8.65        |
| Calcium, . . . .     | 800°    | 1.52        |
| Chromium, . . . .    | ...     | 6.92        |
| Cobalt, . . . .      | 1800    | 8.95        |
| Copper, . . . .      | 1095    | 8.93        |
| Gold, . . . .        | 1064    | 19.30       |
| Iridium, . . . .     | 2500    | 21.15       |
| Iron (pure), . . . . | 1800 ?  | 7.85        |
| „ (cast), . . . .    | 1050    | 7.0 - 7.6   |
| „ (wrought), . . . . | 1500    | 7.25 - 7.79 |
| „ (steel), . . . .   | 1300    | 7.6 - 7.8   |
| Lead, . . . .        | 326     | 11.36       |
| Magnesium, . . . .   | 750     | 1.75        |
| Manganese, . . . .   | 1600    | 7.42        |
| Mercury, . . . .     | - 38.85 | 13.59       |
| Molybdenum, . . . .  | 1800 ?  | 8.6         |
| Nickel, . . . .      | 1600    | 8.25 - 8.8  |
| Platinum, . . . .    | 1775    | 21.4        |
| Potassium, . . . .   | 58°     | 0.875       |
| Silver, . . . .      | 1040    | 10.47       |
| Sodium, . . . .      | 90°     | 0.97        |
| Tin, . . . .         | 230     | 7.29        |
| Tungsten, . . . .    | 1500 ?  | 19.13       |
| Zinc, . . . .        | 418     | 6.86 - 7.2  |

## APPROXIMATE TEMPERATURES.

|                                     |       |
|-------------------------------------|-------|
| Commencement of red heat, . . . . . | 530°  |
| Dark red heat, . . . . .            | 700°  |
| Cherry-red heat, . . . . .          | 850°  |
| Bright red heat, . . . . .          | 950°  |
| Orange-coloured heat, . . . . .     | 1100° |
| Full white heat, . . . . .          | 1500° |

## TEMPERATURE OF SOME FLAMES.

|  |       |
|--|-------|
| Bunsen burner, . . . . .                 | 1870° |
| Acetylene burner, . . . . .              | 2550° |
| Hydrogen flame (free burning), . . . . . | 1900° |
| Coal-gas blowpipe, . . . . .             | 2200° |
| Oxyhydrogen blowpipe, . . . . .          | 2420° |

## FREEZING MIXTURES.

| Substance.   | Parts per 100 parts of Water. | Lowering of Temperature. |
|--|-------------------------------|--------------------------|
| Crystallised calcium chloride, . . . . .           | 250                           | - 12° to - 23°           |
| Ammonium nitrate, . . . . .                        | 60                            | - 13° to - 27°           |
| Ammonium thiocyanate, . . . . .                    | 133                           | - 18° to - 31°           |
| Potassium thiocyanate, . . . . .                   | 150                           | - 23° to - 34°           |
| Ammonium nitrate, . . . . .                        | 45 (ice)                      | - 16.7°                  |
| Sodium chloride, . . . . .                         | 33 „                          | - 21°                    |
| Ammonium thiocyanate and sodium nitrate, . . . . . | 39.5 and 54.5 (ice)           | - 37.4°                  |
| Calcium chloride crystallised, . . . . .           | 1 mol. with 8.5 mol. (ice)    | - 54°                    |
| Hydrochloric acid, . . . . .                       | 1 part, ice 2 parts           | - 32°                    |

## TENSION OF AQUEOUS VAPOUR.

In millimeters of mercury.

| Temperature. | Pressure. | Temperature. | Pressure. |
|--------------|-----------|--------------|-----------|
| 0°           | 4.569     | 22°          | 19.630    |
| 1            | 4.909     | 23           | 20.858    |
| 2            | 5.272     | 24           | 22.152    |
| 3            | 5.658     | 25           | 23.517    |
| 4            | 6.069     | 26           | 24.956    |
| 5            | 6.507     | 27           | 26.471    |
| 6            | 6.972     | 28           | 28.065    |
| 7            | 7.466     | 29           | 29.744    |
| 8            | 7.991     | 30           | 31.510    |
| 9            | 8.548     | 31           | 33.370    |
| 10           | 9.140     | 32           | 35.320    |
| 11           | 9.767     | 33           | 37.37     |
| 12           | 10.432    | 34           | 39.52     |
| 13           | 11.137    | 35           | 41.78     |
| 14           | 11.884    | 36           | 44.16     |
| 15           | 12.674    | 37           | 46.65     |
| 16           | 13.510    | 38           | 49.26     |
| 17           | 14.395    | 39           | 52.00     |
| 18           | 15.330    | 40           | 54.87     |
| 19           | 16.319    | 41           | 57.87     |
| 20           | 17.363    | 42           | 61.02     |
| 21           | 18.466    | 43           | 64.31     |

## ATOMIC WEIGHTS.

Taken from the International Table for 1906.

These numbers are calculated by taking 10 = 16.

|                     |       |                   |       |
|---------------------|-------|-------------------|-------|
| Aluminium, . . . Al | 27.1  | Boron, . . . B    | 11.0  |
| Antimony, . . . Sb  | 120.2 | Bromine, . . . Br | 79.96 |
| Argon, . . . A      | 39.9  | Cadmium, . . . Cd | 112.4 |
| Arsenic, . . . As   | 75.0  | Caesium, . . . Cs | 132.9 |
| Barium, . . . Ba    | 137.4 | Calcium, . . . Ca | 40.1  |
| Bismuth, . . . Bi   | 208.5 | Carbon, . . . C   | 12.0  |

|                              |        |                        |             |
|------------------------------|--------|------------------------|-------------|
| Cerium, . . . Ce             | 140.25 | <b>Oxygen, . . . O</b> | <b>14.0</b> |
| Chlorine . . . Cl            | 35.45  | Palladium, . . Pd      | 106.5       |
| Chromium, . . Cr             | 52.1   | Phosphorus, . . P      | 31.0        |
| Cobalt, . . . Co             | 59.0   | Platinum, . . . Pt     | 194.8       |
| Columbium (Niobium), Cb[Nb]  | 94.0   | Potassium, . . . K     | 39.15       |
| Copper, . . . Cu             | 63.6   | Praseodymium, Pr       | 140.5       |
| Erbium, . . . E              | 166.0  | Radium, . . . Ra       | 225.0       |
| Fluorine, . . . F            | 19.0   | Rhodium, . . . Rh      | 103.0       |
| Gadolinium, . . Gd           | 156.0  | Rubidium, . . . Rb     | 85.5        |
| Gallium, . . . Ga            | 70.0   | Ruthenium, . . Ru      | 101.7       |
| Germanium, . . Ge            | 72.5   | Samarium, . . . Sm     | 150.3       |
| Glucinum (Beryllium), Ge[Be] | 9.1    | Scandium, . . . Sc     | 44.1        |
| Gold, . . . Au               | 197.2  | Selenium, . . . Se     | 79.2        |
| Helium, . . . He             | 4.0    | Silicon, . . . Si      | 28.4        |
| Hydrogen, . . . H            | 1.008  | Silver, . . . Ag       | 107.93      |
| Indium, . . . In             | 115.0  | Sodium, . . . Na       | 23.05       |
| Iodine, . . . I              | 126.97 | Strontium, . . . Sr    | 87.6        |
| Iridium, . . . Ir            | 193.0  | Sulphur, . . . S       | 32.06       |
| Iron, . . . Fe               | 55.9   | Tantalum, . . . Ta     | 183.0       |
| Krypton, . . . Kr            | 81.8   | Tellurium, . . . Te    | 127.6       |
| Lanthanum, . . La            | 138.9  | Terbium, . . . Tb      | 160.0       |
| Lead, . . . Pb               | 206.9  | Thallium, . . . Tl     | 204.1       |
| Lithium, . . . Li            | 7.03   | Thorium, . . . Th      | 232.5       |
| Magnesium, . . Mg            | 24.36  | Thulium, . . . Tm      | 171.0       |
| Manganese, . . Mn            | 55.0   | Tin, . . . Sn          | 119.0       |
| Mercury, . . . Hg            | 200.0  | Titanium, . . . Ti     | 48.1        |
| Molybdenum, . . Mo           | 96.0   | Tungsten, . . . W      | 184.0       |
| Neodymium, . . Nd            | 143.6  | Uranium, . . . U       | 238.5       |
| Neon, . . . Ne               | 20.0   | Vanadium, . . . V      | 51.2        |
| Nickel, . . . Ni             | 58.7   | Xenon, . . . X         | 128.0       |
| Nitrogen, . . . N            | 14.04  | Ytterbium, . . Yb      | 173.0       |
| Osmium, . . . Os             | 191.0  | Yttrium, . . . Yt      | 89.0        |
|                              |        | Zinc, . . . Zn         | 65.4        |
|                              |        | Zirconium, . . Zr      | 90.6        |

In the table representing the periodic system of the elements on the opposite page, the symbols of the elements are printed in heavy and ordinary type, in order to show at a glance those members in each group which have similar properties.

## PERIODIC SYSTEM OF THE ELEMENTS.

| Period. |    | O.                                  | I.               | II. | III.                          | IV.             | V.                            | VI.             | VII.                          | VIII.           |                 |     |
|---------|----|-------------------------------------|------------------|-----|-------------------------------|-----------------|-------------------------------|-----------------|-------------------------------|-----------------|-----------------|-----|
|         |    | Hydrogen<br>Com-<br>pound.          | —                | —   | —                             | MH <sub>4</sub> | MH <sub>3</sub>               | MH <sub>2</sub> | MH                            |                 |                 |     |
|         |    | Highest<br>Oxygen<br>Com-<br>pound. | M <sub>2</sub> O | MO  | M <sub>2</sub> O <sub>3</sub> | MO <sub>2</sub> | M <sub>2</sub> O <sub>5</sub> | MO <sub>3</sub> | M <sub>2</sub> O <sub>7</sub> | MO <sub>3</sub> | MO <sub>2</sub> | MO  |
|         |    | [H]                                 |                  |     |                               |                 |                               |                 |                               |                 |                 |     |
| I.      | 1  | He                                  | Li               | Be  | B                             | C               | N                             | O               | F                             | ...             | ...             | ... |
| II.     | 2  | Ne                                  | Na               | Mg  | Al                            | Si              | P                             | S               | Cl                            | ...             | ...             | ... |
| III.    | 3  | A                                   | K                | Ca  | Sc                            | Ti              | V                             | Cr              | Mn                            | Fe              | Ni              | Co  |
|         | 4  | ...                                 | Cu               | Zn  | Ga                            | Ge              | As                            | Se              | Br                            | ...             | ...             | ... |
| IV.     | 5  | Kr                                  | Rb               | Sr  | Y                             | Zr              | Nd                            | Mo              | ...                           | Ru              | Rh              | Pd  |
|         | 6  | ...                                 | Ag               | Cd  | In                            | Sn              | Sb                            | Te              | I                             | ...             | ...             | ... |
| V.      | 7  | X                                   | Cs               | Ba  | La                            | Ce              | [Pr Nd]                       | ...             | Sa                            | ...             | ...             | ... |
|         | 8  | ...                                 | ...              | ... | ...                           | ...             | ...                           | ...             | ...                           | ...             | ...             | ... |
|         | 9  | ...                                 | ...              | ... | Yb                            | ...             | Ta                            | W               | ...                           | Os              | Ir              | Pt  |
|         | 10 | ...                                 | Au               | Hg  | Tl                            | Pb              | Bi                            | ...             | ...                           | ...             | ...             | ... |
|         | 11 | ...                                 | ...              | Ra  | ...                           | Th              | ...                           | Ur              | ...                           | ...             | ...             | ... |

## PREPARATION OF SOME REAGENTS

**Sulphuretted Hydrogen.**

As sulphuretted hydrogen, either as gas or in the form of its aqueous solution, is often required in general chemistry, as well as in analytical chemistry; a simple apparatus for obtaining it either in the form of gas or as a saturated solution is illustrated below, Fig. 27.

The apparatus consists of a tubulated bottle, A, filled with ferrous sulphide, which has a tubulus on each side, near to the bottom, by means of which it is connected with the reservoir, B, shown in the sketch by the dotted lines. D is a wash-bottle which contains water, the outlet from which is connected with a tube, *d*, passing nearly to the bottom of the bottle, E (capacity 3 to 4 litres), filled with distilled water. From this bottle, E, another tube, *f*, which does not dip below the surface of the water, is connected with the small 'catch' bottle, F. The outlet from the 'catch' bottle

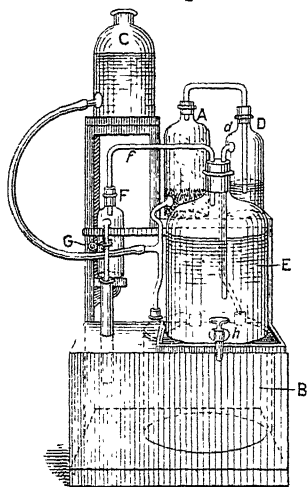


Fig. 27.

is connected by means of a rubber tube with a glass tube 8 or 10 inches long. The rubber can be pinched by the clip, G.

If an aqueous solution of the gas is required, it can be

obtained from the tap, *h*. The gas is obtained by opening the clip, *G*. When the apparatus is newly charged, the clip, *G*, should be opened and a rapid stream of gas bubbled through *E* for a few minutes. This drives out the air on the surface of the water. When all the air is driven out, the clip is closed, and the water will continue to absorb the gas until it is saturated. As soon as the water is completely saturated, the gas pressure drives the acid up into the Reservoir, *C*, and all action ceases. As there is no air in *E*, no oxidation of the sulphuretted hydrogen can take place. All the rubber connections of the apparatus must be carefully wired on, so that no leakage can take place.

To prevent the solution in *E* being driven back into the wash-bottle, should a back pressure be set up, owing to an increase of atmospheric temperature and consequent decrease in solubility of the gas, a layer of mercury—not shown in the sketch—is placed in *D*, below which the tube, *d*, just dips. Hydrochloric acid (1 part acid, 2 parts water) should be used to charge the apparatus.

### Acids.

These should be of 4N. strength. The amounts by volume required can be ascertained by taking the sp. gr. and consulting the curve on p. 10.

**Sulphuric Acid.**—4N. requires 196 grm. per litre.

**Hydrochloric Acid.**—4N., 145.8 grm. per litre.

**Nitric Acid.**—4 N., 252 grm. per litre.

**Acetic Acid.**—4N., 240 grm. per litre.

**Oxalic Acid.**—2N. Dissolve 126 grm. in water and make up to 1 litre.

**Sulphurous Acid.** The saturated solution is about 3.7N.

### Bases.

**Potassium Hydroxide.**—4N., 224 grm. per litre.

**Sodium Hydroxide.**—4N., 160 grm. per litre.

**Barium Hydroxide.**—Prepare a cold saturated solution by shaking up the crystallised  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  until no more is dissolved. Filter from undissolved barium hydroxide and from the carbonate which always contaminates it. The solution is about  $\frac{\text{N}}{3}$ .

**Ammonium Sulphide.**—Saturate 1 vol. ammonium hydroxide with sulphuretted hydrogen, and add 2 vols. ammonium hydroxide of the same strength, and dilute with 5 vols. distilled water.

### Salts.

**Ammonium Chloride.**—4N., 212 grm. per litre.

**Ammonium Sulphate.**—N., 66 grm. per litre.

**Ammonium Oxalate.**—N., 78 grm. crystallised salt  $(\text{NH}_4\text{COO})_2 \cdot 2\text{H}_2\text{O}$  in 1 litre of water.

**Ammonium Molybdate.**—Dissolve 150 grm. ammonium molybdate in 1 litre of water; pour into 1 litre of nitric acid (sp. gr. 1.2). Then dissolve 100 grm. ammonium nitrate in this mixture; allow to stand overnight, and decant from any residue.

**Potassium Chromate.**—N., 97 grm. per litre.

**Potassium Dichromate.**— $\frac{\text{N}}{4}$ , 36.79 grm. per litre.

**Potassium Ferrocyanide.**—N., 105.5 grm. of the crystallised salt  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  per litre.

**Potassium Thiocyanate.**— $\frac{\text{N}}{2}$ , 48.5 grm. per litre.



**Potassium Carbonate.**—4N., 276 gm. anhydrous  $K_2CO_3$  per litre.

**Sodium Carbonate.**—N., 53 gm. anhydrous sodium carbonate per litre.

**Sodium Phosphate.**— $\frac{N}{2}$ , 59.6 gm.  $Na_2HPO_4 \cdot 12H_2O$  per litre.

**Barium Chloride.**—N., 122 gm.  $BaCl_2 \cdot 2H_2O$  per litre.

**Ferric Chloride.**—N., 54 gm. ferric chloride and 5 c.c. conc. HCl per litre.

**Lead Acetate.**—N., 190 gm.  $(CH_3COO)_2Pb \cdot 3H_2O$  per litre.

**Magnesia Mixture.**—Dissolve 50 gm. crystallised magnesium chloride or sulphate in about 200 c.c. water; add 70 gm. ammonium chloride, dissolved separately in 200 c.c. water and 300 c.c. strong ammonium hydroxide. Finally make up to one litre with distilled water and filter if necessary.

**Mercurous Nitrate.**—N. Dissolve 200 gm. mercury in just sufficient moderately strong nitric acid (1:1), and when dissolved, dilute to 1 litre with water. Preserve in a stoppered bottle containing a little metallic mercury. The strength of this reagent is not constant.

**Stannous Chloride.**—2N. Dissolve 225 gm. crystallised stannous chloride in 500 c.c. 4N. hydrochloric acid and dilute to 1 litre with water. Place some fragments of metallic tin in the bottle in which the solution is preserved. The strength of this reagent is not constant.

**Stannic Chloride.**—2N. Take the solution of stannous chloride prepared as above and add bromine water to it until it is just brown. Now heat on the sand-bath until the solution becomes colourless. Make up to 1 litre.

**Fehling's Solution.**—Dissolve 350 gm. Rochelle salt and 100 gm. sodium hydroxide in 500 c.c. water. Also

dissolve 69.28 grm. copper sulphate in 300 c.c. water acidified with  $\frac{1}{2}$  c.c. conc. sulphuric acid. When cool, make up to 500 c.c. When the solution is required, mix equal volumes of the two solutions together. This is better than mixing in the first place, because Fehling's solution deteriorates on keeping.

**Starch Paste.**—Grind up 1 to 2 grm. starch into a thin paste with water. Pour the paste into 150 c.c. boiling water and continue boiling for a few minutes. Allow to stand until cold, and pour off the clear solution. This solution will keep for some weeks if 1 c.c. of chloroform is added to it, but the blue colouration produced by iodine is more intense when it is freshly prepared.

**Litmus Solution.**—Digest 100 grm. litmus with 500 c.c. hot water. Allow to stand overnight, and decant off the clear solution, afterwards filtering if necessary. Now to the clear solution add 300 c.c. methylated spirit and dilute to 1 litre.

**Phenolphthalein.**—Dissolve 5 grm. phenolphthalein in 100 c.c. warm methylated spirit and dilute to 1 litre with a mixture of equal volumes of water and methylated spirit.

**Methyl Orange.**—Dissolve 2 grm. methyl orange in 200 c.c. methylated spirit and dilute to 1 litre with water.

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